DEVELOPMENT OF HYDROGEN SENSORS AND RECOMBINERS

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ABSTRACT

Hydrogen energy is very promising, as it ensures a high efficiency and ecological cleanliness of energy conversion. The goal of the present work is to provide the analysis of hydrogen safety aspects and to prescribe methods of safety operation with hydrogen. The authors conducted a hazard analysis of hydrogen operation and storage in comparison with other fuels. Good ventilation is the main hydrogen operation requirement. Besides, an effective way of protection against propagation of hazards (for instance, leaks) is neutralization of dangerous hydrogen-air mixtures by a method of controlled catalytic combustion inside special devices, so-called recombiners [1-3]. The basis of these devices is a high porosity cell material (HPCM), activated by platinum deposition. Apart from recombiners, HPCM was also applied for development of hydrogen detectors intended for measurement and analysis of hydrogen concentration for hydrogen-driven transport and objects of hydrogen infrastructure (including vapor-air media at high pressure and temperatures). A system of hydrogen safety based on hydrogen detectors and hydrogen catalytic recombiners was developed. Experimental and theoretical studies of hydrogen combustion processes, heat- and mass transfer, and also gas flows in catalytic-activated HPCM, allowed for a design optimization of recombiners and their location. Pilot hydrogen detectors and hydrogen catalytic recombiners were fabricated and their laboratory tests were successfully performed. Thus, it was indicated that on condition of following the appropriate passive and active safety measures, hydrogen is just as safe as the other fuels. This conclusion represents another incentive for a transition to the hydrogen energy.

1. INTRODUCTION

The hydrogen energy is very promising, as it ensures a high performance and ecological cleanliness. However, there is an opinion, that use of hydrogen causes some fears. The goal of the present report is to provide an analysis of hydrogen safety aspects and to prescribe methods of safety operation with hydrogen.

The authors conducted a comparative analysis of hazardous risks of hydrogen and other fuels. First of all, it must be emphasized, that hydrogen has both advantages and disadvantages as far as safety is concerned. In particular, the explosion-hazardous concentration range of hydrogen (4–96 vol. %) is broader, than for other fuels, therefore a special condition for hydrogen operation must be ensured, which, first of all, must incorporate appropriate ventilation. On the other hand, since the diffusion coefficient of hydrogen is much higher, than for other fuels, in case of leakage the concentration remains explosion-hazardous for a non-critical period of time (gasoline, for example, keeps a steam cloud for a longer period). Non-toxicity is another advantage of hydrogen.

Thus, good ventilation is the main requirement for hydrogen operation. Also, a system of hydrogen safety can be developed based on hydrogen detectors (Fig. 1 and 2) and hydrogen catalytic burners, so-called recombiners (Fig. 3).

2. THE SYSTEM OF HYDROGEN SAFETY

2.1. High porosity cell material

The basis of elements of the developed hydrogen safety system is high porosity cell material (HPCM), which is the porous metallic sponge. Such a material consists of hollow cells with a distinctive size of several millimeters and walls coated with thin porous secondary layer of γ-Al_2O_3. The thickness of γ-

Al_2O_3 coating is 20–50 μm, the specific surface square of HPCM with γ-Al_2O_3 layer is 10–25 m^2/g. Thus, HPCM can be characterized with a double porosity:

1) a macroporosity – a ratio between free volume of cells and total HPCM volume;

2) a microporosity – a porosity of HPCM cell walls.

In order to provide catalytic properties, HPCM is coated with the platinum by vacuum deposition method. Advantage of HPCM represents a combination of an expanded catalyst surface with low gas dynamic resistance. High values of a microporosity provide a high specific HPCM surface square and, therefore, ensure a high catalysis performance inside the pores of walls. At the same time the high macroporosity allows a gas flow to pass freely through HPCM plate with a small gas dynamic resistance. Thus, the specific HPCM structure provides a high catalytic activity of catalysts in their basis by means of intensification of heat- and mass transfer processes at rather low specific HPCM surface (10^4 m^2/m^3), which is by 3-4 exponential orders lower, than for the carriers with highly-surface, for example, oxides of aluminum or silicium. In addition, the lower part of HPCM plate was activated by platinum by the method of ionic-magnetron sputtering.

The hydrogen sensors and recombiners have been developed [4-7] based on the experimental and theoretical studies on hydrogen combustion processes, heat- and mass transfer, and also gas flows of in catalytic-activated HPCM. The description and performance data of these devices are shown below.

2.2. Hydrogen recombiners

2.2.1. Description of hydrogen recombiners

An effective way of protection against dangerous propagation of hazards (for instance, leaks) is a neutralization of hazardous hydrogen-air mixtures by a method of controlled catalytic combustion in special devices, so-called recombiners. The system of rationally distributed recombiners ensuring the safety conditions could be developed for different applications (for instance, cars or buildings). The basic principle is the following: if hydrogen combustion rate were sufficient versus a hydrogen feed, then it's concentration would not exceed fire hazardous limits.

The developed recombiner consists of a convective case and the catalytic element (HPCM plate located in the removable cartridge) mounted into the lower part of convective case. The convective case is designed as a rectangular (Fig. 3) or circular pipe. The Grids protect case inlet and outlet (to prevent the ambient media from ignitions). The convective case is placed upright so that it makes a natural convection ("the chimney effect").

When the hydrogen concentration exceeds a critical level (for hydrogen-air mixes more than 0.7 vol. % at the ambient temperature) the activated HPCM spontaneously starts oxidizing the hydrogen. It causes a spontaneous heating of a catalytic element and convective circulation of gas mixture through a recombiner. Thus, the recombiner operates automatically without external energy source or control facilities. Recombiner productive capacity depends on it's dimensions and can be calculated on the basis of a developed physical model of such devices (see below). So, for example, at the height of a convective case about 1 m, the linear speed of air circulation exceeds 1 m/sec. The productive capacity can be substationally increased by using an additional heating element located in the bottom of the recombiner case.

Thus, the problem of hydrogen-air mixtures neutralization was resolved by means of hydrogen recombiners based on HPCM. The system of passive hydrogen safety was developed on their basis.

For methane-air mixtures the catalytic combustion starts at elevated temperatures (about 400°C) only. Therefore the catalyst must be pre-heated. However, with an introduction of methane, the process of catalytic combustion will accelerate as a result of heating caused by methane oxidation. Thus, it is possible to develop methane catalytic recombiners.

Figure 1. The photo of hydrogen sensor.

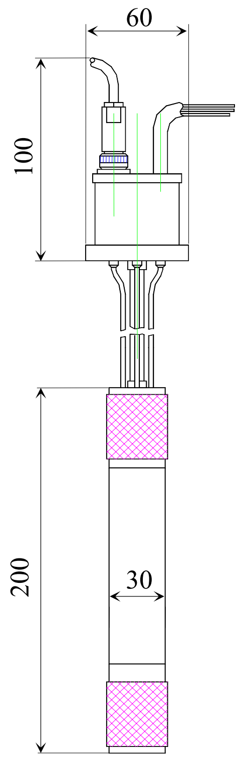

Figure 2. The basic dimensions of hydrogen sensor.

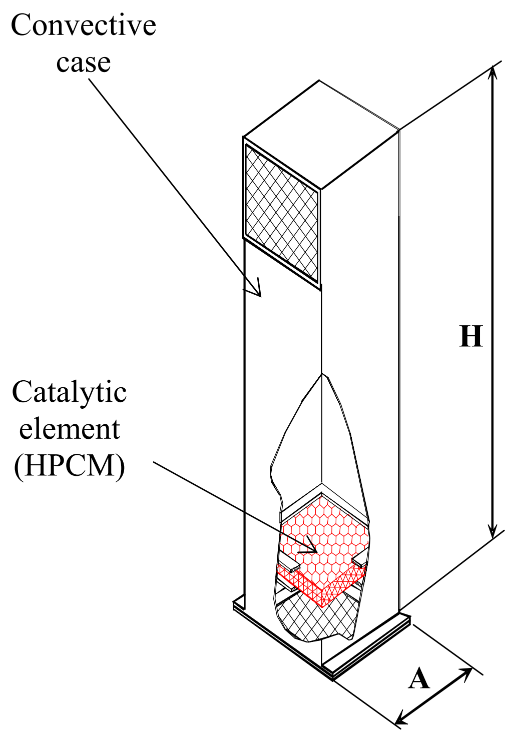

Figure 3. Catalytic hydrogen recombiner.

2.2.2. Theoretical model of hydrogen recombination

Let's consider stationary moving of air in a vertical pipe (chimney) of recombiner with cross section S and height H, at which bottom is placed a thin HPCM plate. Air with a volumetric hydrogen contents C enters from bottom of convective case with speed U_o at temperature T_o, heats up to temperature T as a result of an oxidizing of a part of hydrogen in a HPCM volume and, accordingly, is accelerated up to speed U.

An equation of continuity:

$$\rho_0 U_0 = U\rho,$$

where ρ_0 and ρ - density of "cold" and heated air.

The change of density is bound to change of temperature:

$$\rho = \frac{\rho_0 T_0}{T}.$$

Increase of temperature of an air flow owing to recombination of hydrogen (C_0-C):

$$\Delta T = T - T_0 = \alpha(C_0 - C),$$

where α=83.5 K/1%vol.

In stationary flow the total forces acted on an air pole in a recombiner, is equal 0. From the most common reasons follows, that in this case pressures drop on a HPCM volume is defined by the formula:

$$\Delta p = p_2 - p_1 - g\int_0^H \rho dz - \frac{\Sigma F_{mp}}{S}.$$

In this formula p_2-p_1 – pressure difference between top and bottom the pipe, $\frac{\Sigma F_{mp}}{S}$ - total of frictional forces of air pole about a chimney wall. As is known from the theory and practice of convection calculations in an atmosphere, the pressure on an inlet and outlet of a pipe coincides with atmospheric, varying on height z under the law:

$$p = p_0 + \rho_0 gz,$$

thus $\Delta p_a = p_2 - p_1 = \rho_0 gH\Delta T/T$.

Let's neglect cooling of an air flow in a pipe, for example, in case of application of heat isolating convective case, and also all gas dynamics resistance, supposing by their small in matching with a HPCM resistance.

In this case ρ=const on height of a chimney:

$$\Delta p = gH(\rho_0 - \rho) = \rho_0 gH(T - T_0)/T_0,$$

$$\Delta p = \rho_O gH\frac{\alpha\Delta c}{T_O + \alpha\Delta c},$$

$$T = T_0 + \alpha\Delta C.$$

Owing to presence of such pressure drop air transits through a HPCM volume, overcoming its resistance it is known from experiment:

$$\Delta p_g = A v^n (1+\beta\Delta T).$$

where A, H and β - experimental constants for concrete size of a HPCM in real conditions of a hydrogen oxidizing.

$$\Delta T = \alpha(C_0 - C).$$

Thus

$$\rho_o g H \frac{\alpha\Delta c}{T_o + \alpha\Delta c} = A \cdot v^n \left[1 + \beta \cdot \alpha\Delta c\right].$$

Rate of flow:

$$V = \left(\frac{\rho_o g}{A}\right)^{1/n} \cdot H^{1/n} \frac{\alpha\Delta c}{(T_o + \alpha\Delta c)\cdot(1+\beta\alpha\Delta c)}.$$

Apparently a recombiner productive capacity, i.e. speed of hydrogen burning:

$$Q = SV\Delta C.$$

In real conditions of the hydrogen recombination process in used HPCM samples the complete hydrogen burning was observed practically. In this case:

$$Q = S \cdot \left(\frac{\rho_o g}{A}\right)^{1/n} H^{1/n} \cdot C \frac{(\alpha c)^{1/n}}{T_o (1 + \frac{\alpha c}{T_o}) \cdot (1 + \beta\alpha \cdot c)}.$$

The obtained formula defines, apparently, maximal productivity of a concrete recombiner with concrete samples of a HPCM.

Detailed comparison of mentioned theoretical approach with experimental data will be provided in a future and published separately.

2.2.3. Experimental samples of hydrogen recombiners

Provided tests of pilot samples of recombiners have shown rather good correlation of experimental data with model calculations. Parameters, quantity and the scheme of recombiners disposition for different spaces have been calculated taking into consideration possible scripts of emergencies development with hydrogen leaks. The typical most acceptable sizes of recombiners are shown in Table 1.

Table 1. Parameters of developed hydrogen recombiners.

Model of recombiner	**Dimensions of recombiner, $A\times H$, mm×mm**	**Productivity, m^3/h (for 4 vol. % of H_2)**
1	100×300	1.35 (figure 4)
2	200×1000	7.5 (evaluation)
3	500×3000	100 (evaluation)

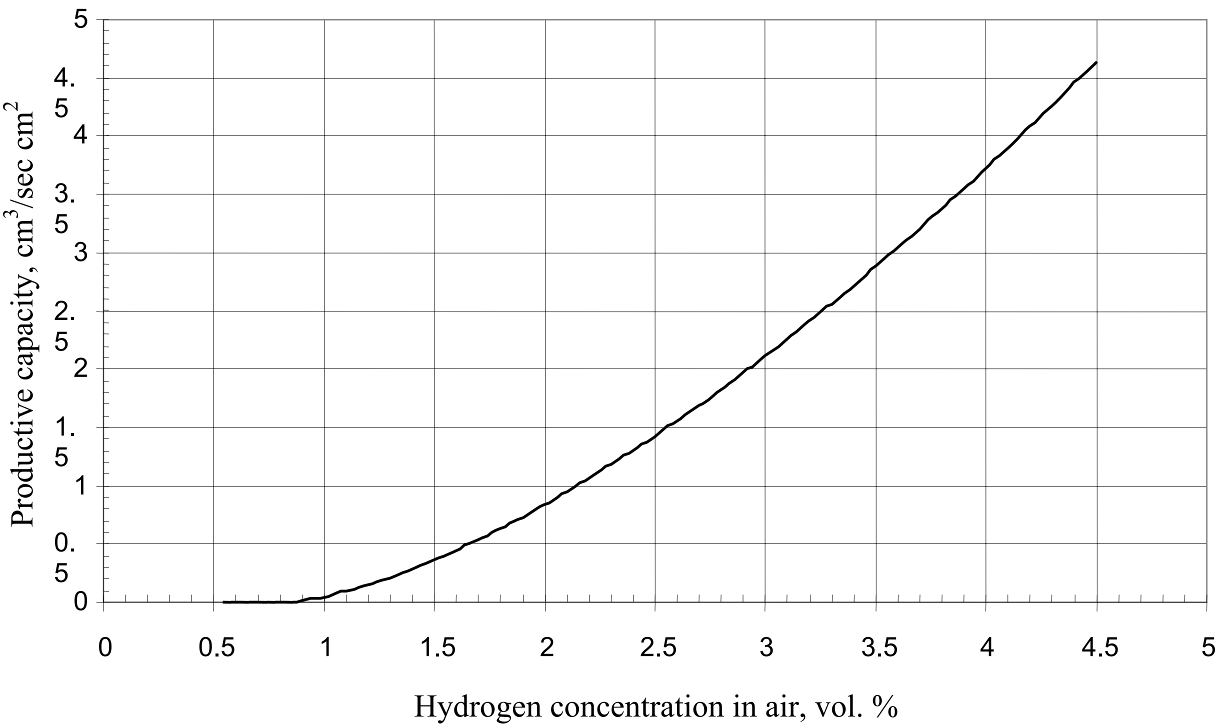

Figure 4. Experimental dependence of productivity of recombiner model 1 upon hydrogen concentration in air.

2.3. Hydrogen sensors

Developed hydrogen sensors are intended for measurement and analysis of hydrogen concentration in different conditions, including vapor-air media at high pressure and temperatures. The measuring system includes thermocatalytic hydrogen detectors made with use of HPCM technology and the multichannel complex device base on PC AT for the collection and automated processing of signals.

The basic idea of a given detectors design based on measurements of a temperatures difference between an ambient media and disk HPCM element activated by platinum, through which one convective flow of analyzed gas passes. For temperatures measurements the standard thermocouples in stainless steel tube were used.

All the elements of the detector are located within the cylindrical protective case (Fig. 1, 2 and 5), the inlet and outlet of which one is protected by a metal grid. A basis of the secondary device of the detectors is the LCARD system of signals processing connected with the PC AT. Several detectors can be simultaneously connected with the system. The program of signals processing calculates temperatures of an active element, of a comparative metal grid and heater, and on the basis of these data outputs H_2 concentrations. During measurements the analysis of the signals permitting to reveal failures is provided also. The sensor has no open current-transfer parts to exclude initiation of ignitions or knockings of hydrogen in critical situations. Measurements of O_2 concentration in H_2, temporary placing of the detector in water and self-testing are possible.

Technical performances confirmed by tests:

- temperature of analyzed media ≤ 600°C;
- operating pressure up to 25.0 MPa;
- pressure of water vapour up to 0.3 MPa;

- relaxation time ≈ 10 sec;

- a range of measured hydrogen concentration from 0 up to 100 vol. %;

- accuracy of measurements: 5% for 0–4 vol. % range;

  10% for 4–80 vol. % range;

  15% for ≥ 90 vol. % range;

- the bottom limit of sensitivity 10^{-2} vol. % of H_2.

Thus the principle of sensors operation and their design were developed, pilot samples were made and laboratory tests were provided.

3. CONCLUSIONS

The hazard analysis of hydrogen operation and storage was performed.

The model of hydrogen recombiner was developed. This model allows to calculate recombiners capacity dependant on recombiner design parameters (height and cross section of the recombiner).

The validity of the model was tested with use of gas dynamic stand for research of the characteristics of HPCM. Gas dynamic characteristics of several catalytic HPCM –based units were measured in a broad range of pressure drops.

A hydrogen safety system, which can be used for transporting hydrogen and objects of hydrogen infrastructure, was developed. Also the system can be applied for atomic power stations and gas industry for the identification and elimination of hydrogen leaks (development of sensors and catalytic burners for methane and other gas fuels is also possible). Pilot hydrogen sensors and hydrogen catalytic recombiners were made (see Fig. 5) and their laboratory tests were successful.

Thus, with appropriate passive and active safety measures being ensured, hydrogen is just as safe as the other fuels. This conclusion represents another incentive for a hydrogen energy development.

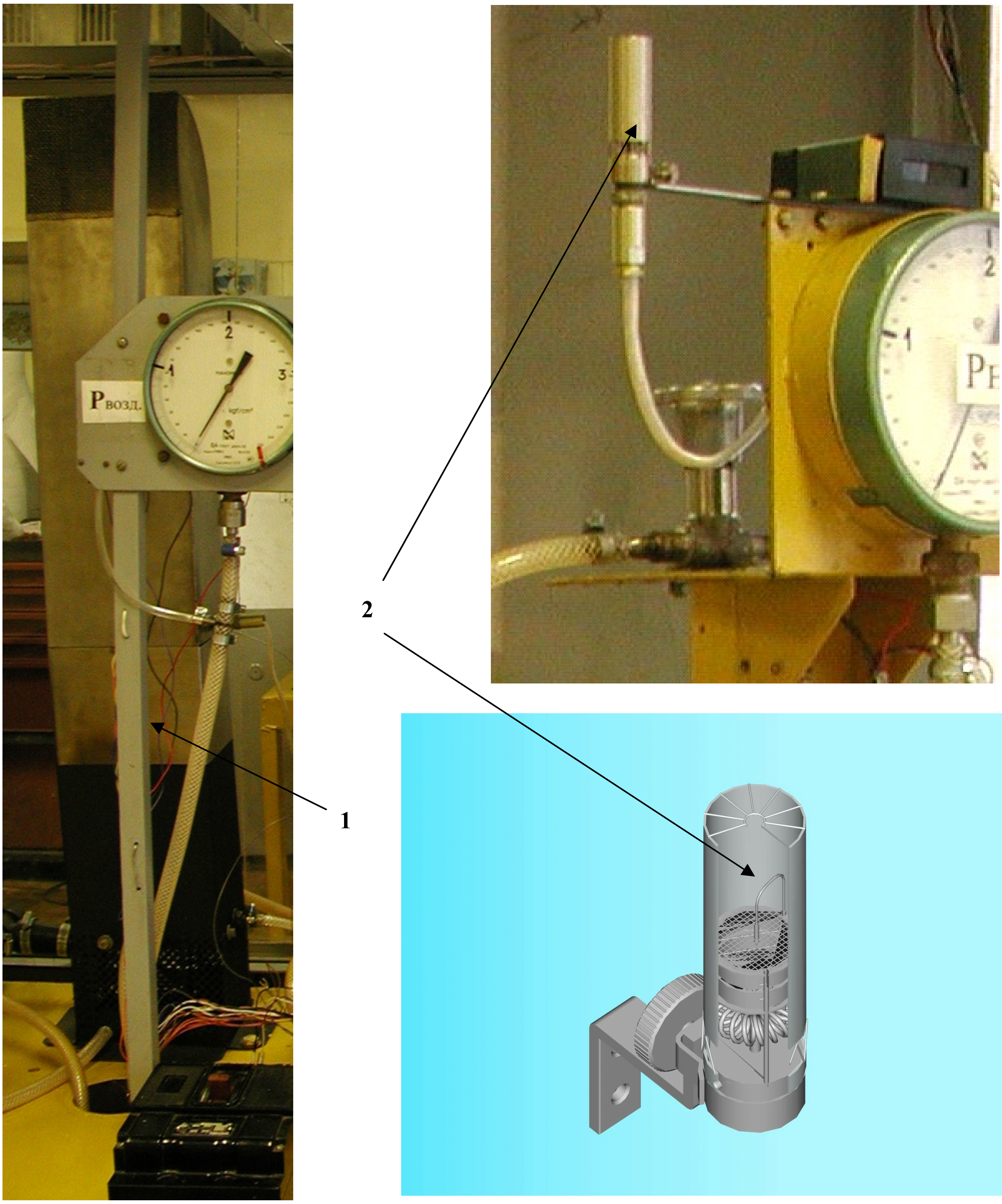

Figure 5. The elements of hydrogen safety system (recombiner (1) and hydrogen sensor (2)).

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