ABSTRACT:

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. The aim of this paper is development of hydrogen detectors and hydrogen catalytic recombiners based on high porosity cell material (HPCM). Experimental and theoretical studies of hydrogen combustion processes, heat- and mass transfer in catalytic-activated HPCM, allowed for a design optimization of recombiners and detectors and their location. Pilot hydrogen detectors and hydrogen catalytic recombiners were fabricated and their laboratory tests were successfully performed.

KEYWORDS: Hydrogen safety, combiner, detector, high porosity cell material, modeling.

1. Introduction

The hydrogen energy is very promising, as it ensures a high performance and ecological cleanliness. However, there is an opinion, that the use of hydrogen causes some fears. One important issue is the prevention of the formation of ignitable mixtures of hydrogen inadvertently released into an oxygen containing atmosphere in all hydrogen application fields like production, storage and utilization. An effective way of protection against propagation of hazards is neutralization of dangerous hydrogen-air mixtures by a method of controlled catalytic combustion inside special devices, so-called recombiners. The authors conducted an analysis and tests of a pilot sample of so-called Passive Auto-catalytic Recombiner (PAR) based on a technology of using High Porosity Cell Materials (HPCM) as catalytic devices for such recombiners. The authors in addition developed the experimental testing stand for measuring the properties of individual HPCM catalytic samples in order to achieve maximal productivity in projected PARs. The authors also conducted the development and tests of hydrogen sensors based on the same technology of using HPCM catalytic plates as the proposed PARs. The synergetic effect caused by using the same technology in hydrogen recombiners and sensors promises to introduce new effective and low cost hydrogen safety systems in many hydrogen energy industrial applications.

2. Passive auto-catalytic combiner on the basis of HPCM for hydrogen safety systems.

In the constructions of PARs an important role is played by catalytic devices providing an effective low temperature oxidation of hydrogen at a low hydraulic resistance to passing gas flow. The internal cartridges of flat catalytic plates activated by platinum catalyst are widely used in many traditional types of PARs nowadays. However, a regular geometrical arrangement of such catalytic plates results in the formation of boundary layers and, accordingly, to aggravation of processes of heat and mass transfer and incomplete combustion of hydrogen.

In this connection High Porosity Cell Material (HPCM) activated by platinum catalyst deposition seems to be more preferable base for catalytic devices of passive recombiners than regular catalyst sheets. Such materials represent a distribution of hollow millimeter cells in a porous metallic sponge (stainless steel or nickel alloy) and have double porosity distribution. Along with macroporosity of sponge cells there is also microporosity of the cell walls of thin porous secondary layer from $\gamma$-Al$_2$O$_3$ on which platinum catalyst is deposited. High values of microporosity ensure a larger specific catalyst surface of HPCM-based passive recombiners than for usual passive recombiners based on regular catalyst sheets and, therefore, high performance of catalysis inside the pores of cell walls. At the same time high macroporosity allows a flow of gas mixture to transit freely through a plate of HPCM at a low gas dynamical resistance. The complete burning of passing hydrogen becomes possible at low hydrogen concentrations in air (less than 4% volumetric).

The developed combiner 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. 1) or circular pipe. The grids protect the 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 ambient 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 the recombiner. Thus, the recombiner operates automatically without external energy source or control facilities.

Recombiner productive capacity depends on its dimensions and properties of its catalytic devices and can be calculated on the basis of a developed physical-chemical model of such devices. The basis of this model (along with usual lows of stationary gas dynamics in the case open to atmosphere at lower and higher ends) is the experimentally derived dependence for pressure drop on HPCM flat sample:

\[ \Delta p_g = A \nu^n (1 + \beta \Delta T) \]

where \( A, n \) and \( \beta \) - experimental constants for concrete size of a HPCM sample in real conditions of a hydrogen oxidizing. \( \Delta T \) – temperature change of gas flow passed through HPCM sample with velocity \( \nu \). So a recombiner productive capacity \( Q = SvC \), i.e. speed of hydrogen burning can be obtained as:

\[ Q = S \cdot \left( \frac{\rho_0 g^2}{A} \right)^{\frac{1}{n}} \cdot H^{\frac{1}{n}} \cdot C \left( \frac{\alpha c}{T_o} \right)^{\frac{1}{n}} \cdot \frac{T_o (1 + \frac{\alpha c}{T_o}) \cdot (1 + \beta \alpha \cdot c)}{ \left( 1 + \beta \Delta T \right) } \]

where \( S \) and \( H \) – recombiner case cross section and height, \( C \) – hydrogen concentration at inlet of the recombiner (at outlet it is supposed to be nearly zero). \( \rho_0, T_0 \) - density and temperature of ambient air-hydrogen mixture, \( \alpha = 83.5 \) K/1%vol – temperature change for unit change of hydrogen concentration.

In order to provide the calculation of productivity of concrete recombiner the parameters \( A, n \) and \( \beta \) of individual HPCM samples must be obtained. For this purpose the authors developed the testing stand (Fig.2) for HPCM samples where the specific parameters of individual samples can be measured at pressures of air-hydrogen-water steam mixture flow from 0.1 up to 0.4 MPa. Fig.3 shows the dependences of pressure drop for various HPCM samples when hydrogen concentration is lower than low limit of recombiner ignition and so \( \beta = 0 \).

Detailed comparison of mentioned theoretical approach with experimental data obtained on pilot samples of recombiners of proposed types will be provided in a future and published separately.

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. In order to start detection from low (10\(^{-2}\) vol. %) hydrogen concentrations there is special spiral heater inside the detector.

All the elements of the detector are located within the cylindrical protective case (Fig. 4 and 5), the inlet and outlet of which 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 through USB-interface. Several detectors can be simultaneously connected with the system. The program of signals processing calculates temperatures of the active element, of the comparative metal grid and heater, and on the basis of these data outputs H\(_2\) concentrations. Technical performances confirmed by tests:
- temperature of analyzed media \( \leq 700^\circ\text{C} \);
- operating pressure up to 25.0 MPa;
- pressure of water vapour up to 0.3 MPa;
- relaxation time \( \approx 10 \) sec;
- a range of measured hydrogen concentration from 10\(^{-2}\) vol. % to 100 vol. %;

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

4. Conclusions

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

For measurement of HPCM samples individual characteristics the gas dynamic stand was developed with the expectation of real conditions of passive recombiner functioning on temperature, pressure and water steam concentration.
Pilot hydrogen sensors, specially designed for hydrogen safety systems, were developed on the same HPCM technology as recombiners. Their laboratory tests were successful.

The developed hydrogen recombiners and sensors on HPCM-technology can be the main part of perspective hydrogen safety system with low cost and high efficiency.

REFERENCES

Fig. 1. Catalytic hydrogen recombiner.
Fig. 2. The experimental stand for measuring HPCM sample characteristics.

Fig. 3. Dependences of pressure drop for various HPCM samples (1 x 10 x 15 cm) of gas flow rate.
Fig. 4. Basic dimensions of hydrogen sensor.
Fig. 5. Elements of hydrogen safety system (recombiner (1) and hydrogen sensor (2)).