SAFE TESTING OF CATALYTIC DEVICES IN HYDROGEN-AIR FLOW

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ABSTRACT

Any experimental study of catalysts and catalytic recombining devices for removal of hydrogen gas from industrial environments is known to carry a risk of ignition of hydrogen. Experiments conducted in an atmosphere with a high concentration of hydrogen present a particular danger.

Here, a technique is reported that allows conducting such experiments with relative safety. This technique has been developed and applied by the company 'Russian Energy Technologies' for the last five years without any significant incident.

A "Gas stream method" for testing and analysis of the characteristics of a catalyst for hydrogen/oxygen recombination is proposed. Tests with a variety of catalysts in a passive recombining device were carried out in a climatic chamber (86 l in volume) with a hydrogen/air mixture containing up to 20% (v/v) hydrogen flowing through it. The balance equation for hydrogen and oxygen flows entering, reacting and exiting the chamber led to a formula for calculating the efficiency of a catalyst or a catalytic device under stationary conditions.

Fluctuations in local temperatures of the catalyst and other parts of the chamber along with variation in the concentration of hydrogen gave the authors an insight into the thermal regime of an active catalyst. This enabled them to develop new catalysts for removal of hydrogen from the environment using industrial recombining devices.

1. INTRODUCTION

Experiments conducted in environments containing hydrogen gas always carry a risk of unexpected ignition and explosion. This report concerns a particular risk associated with testing catalysts for recombination of hydrogen and oxygen, which proceeds as an exothermic reaction leading to overheating of the catalyst and ignition of hydrogen.

$$2H_2 + O_2 \rightarrow 2H_2O \text{ (gas)} + 244.9 \text{ kJ/mole} \tag{1}$$

"Passive autocatalytic recombiners" (PARs) are widely used in nuclear power stations for removal of hydrogen from water-cooling circuits under normal and catastrophic failure conditions [1]. Because the heat of reaction (see eq. (1)) initiates the conversion of hydrogen in PARs, it is important to find an optimal catalytic device that avoids overheating of the catalyst while maintaining a high efficiency of conversion. Testing such catalysts at high concentrations of hydrogen is vital in order to determine the range of conditions at which catalysts and recombining devices are reliable and safe to use.

This report describes a technique for this kind of experiment. The technique has been developed in the last five years by the company 'Russian Energy Technologies' and applied in the search for more effective catalytic structures that can be used in various industrial environments, and, in particular, in hydrogen safety systems at nuclear power stations. The analytical method developed and described below is based on the formula (9) for the efficiency of hydrogen/oxygen recombination under

stationary conditions of gas exchange in the space inside a catalytic cartridge. The results of experiments with various catalysts are reported in [2].

2. EXPERIMENTAL TECHNIQUE

Fig.1 shows a diagram of the climatic chamber (CC) for testing catalysts and catalytic devices. Fig.2 shows a photograph taken at the moment of insertion of the catalytic recombining device into the CC. The cylindrical housing of the chamber with double casing (1, 3) was made of stainless steel sheets 1.5 mm thick. The heat insulation (4) was placed between the walls. The housing was fastened on a rectangular base (2), which contained bath circulator pipes. The CC (86 l in volume) was situated in a draft cupboard away from any combustible materials.

The catalyst samples to be tested, i.e. individual catalytic plates (12) and cartridges of plates in a small-scale recombiner (11), were suspended under the cover of the hatch (8) in the middle part of the CC.

The insert (Fig.1, top left corner) shows a diagram of the recombining device with a 4-plate cartridge. Contact thermocouples were connected to one of the plates in its lower, middle and upper parts. Another thermocouple measured the temperature above the plates. Thus, the thermal regime of the working device was established by reading local temperatures of the catalyst and of the gas exiting the recombiner.

The CC was equipped with the following parts and devices:
- bath circulator with pipes (7, 20, 21) for thermostatic control of the CC,
- gas flow inlet (15) connected with air/ hydrogen mixer (14) and outlet pipe (16),
- two fans (9) to provide gas circulation in the CC,
- hydrogen analyzer (17),
- thermocouples (13),
- two valves (10) for the release of pressure in case of hydrogen ignition.

Signals from thermocouples and a hydrogen analyzer were converted by data acquisition hardware and software system, and changes in hydrogen concentration and local temperatures with time were displayed on a monitor (see Fig.3, as an example).

Thermostatic control was maintained by using a spiral tubular heat exchange element (7) connected to a Julabo Labortechnic GmbH bath circulator with external circulation. Water was used as a heat-carrier for temperatures between 25^0C and approx. 80^0C. Other liquids (oils etc.) had to be used in order to reach temperatures higher than 80^0C in the CC. As the catalytic cartridge is an intensive source of heat itself, the use of a thermostat with a thermocouple installed inside the CC is recommended. For the same reason, heating of the inner space of the CC by electric elements cannot be used for its thermostatic control.

Hydrogen and air were mixed in (14) with two gas flows entering the mixer under controlled rates, hydrogen from a pressurized gas bottle and air from the oil-less piston compressor Durr-Technik V-038. The mixed gas with the required concentration of hydrogen was fed into the CC through a 2 m long plastic pipe and fitted inlet pipe (15) with 15 holes in it (each hole was 2 mm in diameter). To achieve even distribution of gas in the CC, the inlet pipe in the shape of a semi-circle was placed at the very bottom, under one of the two fans with a power 3-5 W situated inside the CC (9).

Gas was let out of the CC through ten vertically fitted pipes (16) placed alongside the inner CC casing, and released into the draft cupboard.

The analysis of hydrogen in the CC was carried out continuously with the use of a pump, which sucked gas into the analyzer (17) through the pipe (18) and returned gas into the CC through the pipe

(19). The analysis was conducted using an electrochemical cell where hydrogen was oxidized on the Pt cathode. The analyzer was manufactured by the company Alfa Bassens (Moscow).

Following both planned and sudden explosions in the CC the pressurized gas was released through two emergency film-type valves (10) with an area of 100 cm^2 each. As a safety measure, a sheet of stainless steel (100x100 cm) was placed between the operator and the CC. The blast wave was largely extinguished at a distance of 2-3 m from the CC. Therefore, the ceiling and walls around the CC did not require any additional protection or reinforcement. Nevertheless, any combustible materials and objects were removed from close proximity to the CC, which was not situated near a window.
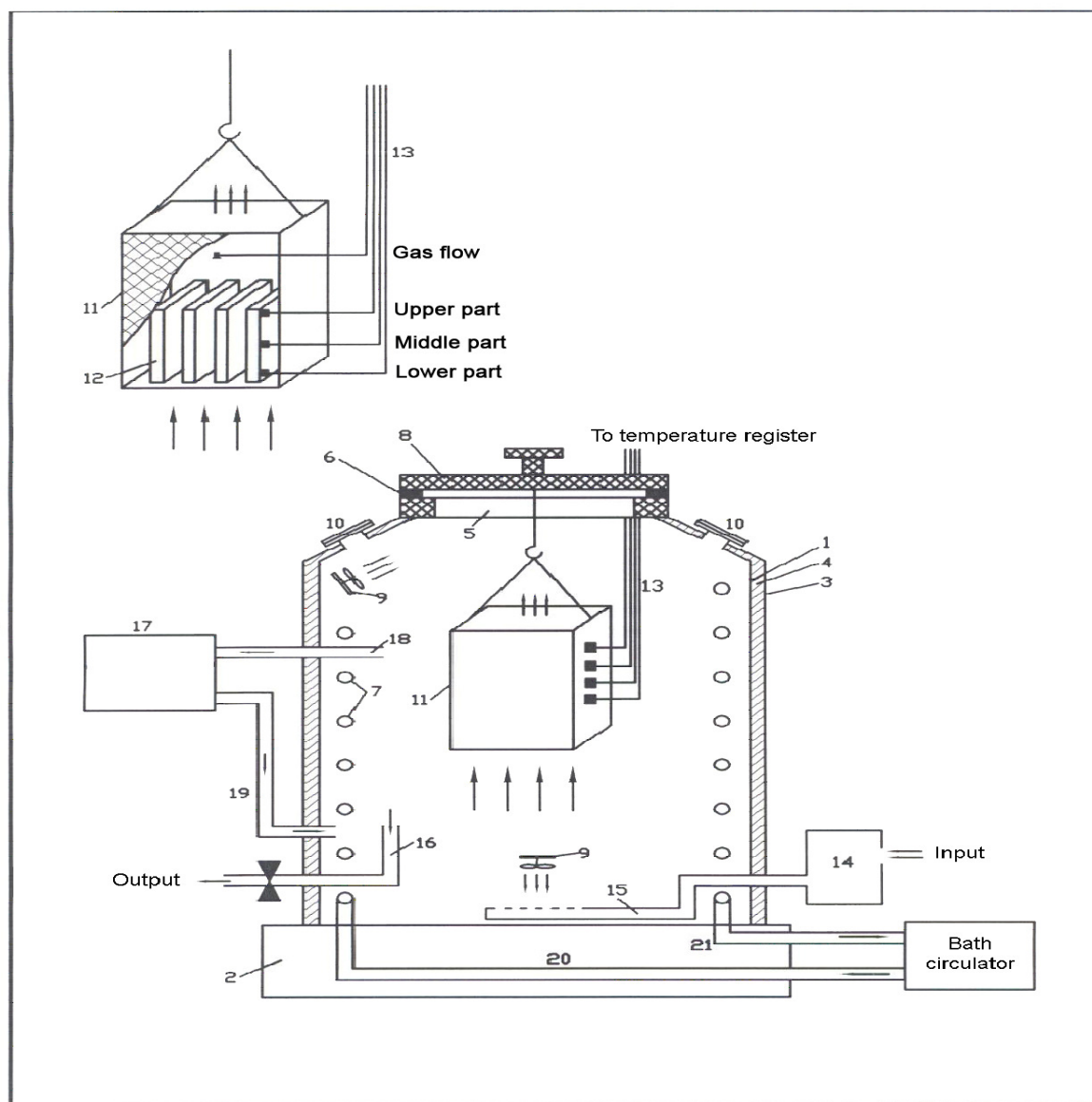

Fig.1. Drawing of the climatic chamber with the insert in the top left corner showing a recombiner with a cartridge of lamellar catalytic plates.

1 – inner casing, 2 – base of CC housing, 3 – external casing, 4 – heat insulation, 5 – basic hatch, 6 – rubber packing, 7 – spiral tubular heat exchange element, 8 – hatch cover, 9 – fans, 10 – gas release valves , 11 – recombiner, 12 – catalytic plates, 13 – thermocouples, 14 – gas mixer, 15 – gas inlet pipe, 16 – one of gas outlet pipes, 17 – hydrogen analyzer, 18 – analyzer inlet suction pipe, 19 – analyzer outlet pipe, 20 and 21 – bath circulator inlet and outlet pipes.

Fig.2. View of the climatic chamber at the moment of insertion of the recombiner.

When the concentration of hydrogen exceeds 15 % v/v, uneven distribution of the initial burning of hydrogen in the enclosed space of the CC, with all the objects inside it, can transform the deflagration regime into detonation, accompanied by a blast wave at a temperature more than 1000^0C [3]. Nevertheless, our long-term experience in such experiments proved that, if the volume of the CC does not exceed 100 l and the concentration of hydrogen is kept below 20 % v/v, the release of the blast wave does not present significant danger provided that the following protective measures are implemented:

1. A protective screen (metal sheet 100x100 cm^2) is placed between the operator and the CC.
2. The operator is wearing a protective face mask.
3. Any peripheral equipment connected to the CC via gas pipes, e.g. gas mixer (14) and hydrogen analyzer (17), is secured in order to avoid it being damaged and becoming a source of flying debris. The gas mixer (14) presents a particular danger, as the concentration of hydrogen in it can reach up to and above 30 % v/v. For that reason, the gas mixer should not be larger than 60 ml in volume. In order to make it secure, the gas mixer should be wrapped in a strong fabric and a metal net. The gas pipes and connections outside the CC should be made of rubber or reinforced plastic of internal diameter not more than 7 mm. The pipes should be at least 2 m long. In our experience, pipes with these specifications prevent the spread of hot plasma outside the CC.

3. FORMULA FOR EFFICIENCY OF THE CATALYTIC CARTRIDGE

The way to define the efficiency of a catalytic device, suggested below, is based on the formula which connects the rate of the catalytic reaction (see eq.(1)) with the air flow (I_{air}) and the hydrogen flow (I_{hy}) entering the CC, when the stationary concentration of hydrogen (C_{stat}) in the CC is reached.

If both flows are entering a gas mixer with constant speed, the concentration of hydrogen (C_{hy}) in the flow that exits the gas mixer is

$$C_{hy} = 100\, I_{hy} /(I_{hy} + I_{air}) \tag{2}$$

In the CC some hydrogen reacts with oxygen inside the recombiner (I_{cat}) and the rest ($I_{hy(out)}$) leaves the CC together with nitrogen (I_N) and oxygen ($I_{ox(out)}$). The corresponding balance equation for hydrogen with respect to time τ looks like

$$I_{cat} /d\tau = I_{hy} /d\tau - I_{hy\,(out)}/d\tau \tag{3}$$

On reaching a stationary condition, when the temperature in the CC and all other kinetic variables cease to change, the rate of hydrogen recombination (or equivalent rate of water vapour formation) can be expressed as a difference in the rates of hydrogen entering and exiting the CC.

$$I_{cat} = I_{hy} - I_{hy(out)} \tag{4}$$

Under stationary conditions, the concentration of hydrogen exiting the CC is the same as the concentration of hydrogen inside the CC (C_{stat}). As the gas exiting the CC consists of nitrogen I_N, oxygen $I_{ox(out)}$ and hydrogen $I_{hy(out)}$ the last may be expressed as

$$I_{hy\,(out)} = (I_N + I_{ox(out)} + I_{hy\,(out)}) (C_{stat}/100) \tag{5}$$

After simple algebraic transformations the formula for $I_{hy(out)}$ is

$$I_{hy(out)} = (I_N + I_{ox(out)})(C_{stat} /100) \{1 - C_{stat} /100\}^{-1} \tag{6}$$

Substitutions $I_{ox(cat)} = 0.5\, I_{cat}$ (according to equation (1)) and $I_{ox(in)} = 0.21\, I_{air}$ in value $I_{ox(out)}$ give us

$$I_{ox(out)} = I_{ox(in)} - I_{ox(cat)} = 0.21\, I_{air} - 0.5\, I_{cat} \tag{7}$$

Now, after substituting equation (7) into equation (6) and some algebraic transformations we obtain the following equation

$$I_{hy(out)} = \frac{(0.79\, I_{air} + 0.21\, I_{air} - 0.5\, I_{cat})(C_{stat} /100)}{1 - C_{stat} /100} = \frac{I_{air} - 0.5\, I_{cat}}{(100/ C_{stat}) - 1} \tag{8}$$

The substitution of (8) into (4) and further transformations gives us the final formula for I_{cat}

$$I_{cat} = \frac{I_{hy} - I_{air} / \{(100/C_{stat}) - 1\}}{1 - 0.5/\{ (100/C_{stat}) - 1\}} \tag{9}$$

If the thermodynamic conditions of gas entering and exiting the CC are the same, I_{cat} may be expressed as volume against time, e.g. l/min. Otherwise, mass or gram-mole against time should be used, e.g. kg/hour, gram-mole/min. In addition, in order to compare the catalytic activity of different

recombining devices (under conditions of natural convection) the unit used is the recombination rate per square section of gas flow, e.g. kg/h м², ml/min cm² [4].

4. DATA PROCESSING AND ANALYSIS

In this final part we describe how the experimental data were analyzed. In particular, in order to study the relationship between catalyst efficiency (recombination rate) and hydrogen concentration, an incremental increase (or reduction) in the concentration of hydrogen in the gas flow entering the CC was required, waiting after each increase (or reduction) for the stationary mode of the catalytic process to be reached. Such an experimental regime was necessary because the formula described above for the efficiency of a catalytic cartridge applies only when the hydrogen-oxygen recombination process is in the stationary phase.
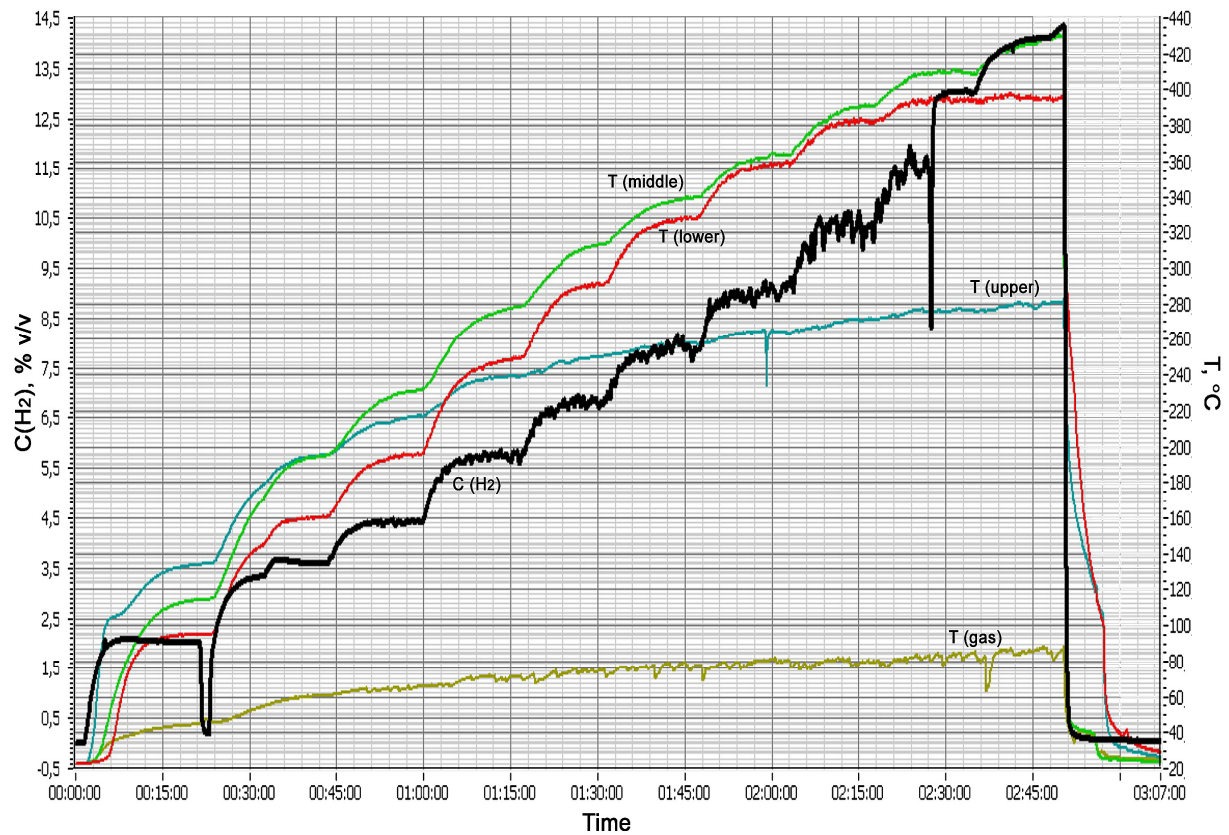

Fig.3. Data from a typical test of a recombining device in the CC.

Fig.3 shows the change in hydrogen concentration inside the CC and   temperatures at four locations (registered by thermocouples (13) – see Fig.1) with time. In this test a cartridge of four catalytic plates (20x3.8 cm in size), which were covered by metal grid at 1/3 of their length, was placed in the recombining device (35x4x4 cm in size). This was typical of many experiments carried out by the authors in their search for a catalyst that is effective at high concentrations of hydrogen [2].

It can be seen from Fig.3 that incremental changes in $C(H_2)$ were followed by simultaneous changes in local temperatures, with the exception of T(gas). Note that for this particular catalyst the highest temperature develops in the middle part of the catalytic plate, and the lowest one in its upper part. The recording ends with the ignition of hydrogen at $C(H_2)$ 14.35 % v/v. At this concentration of hydrogen the temperature in the middle part of the plate has reached 430⁰C, and the efficiency of the catalytic device has peaked at 24 g hydrogen/hour (specific efficiency 1.5 g/h cm²). The abrupt fall in local

temperatures and hydrogen concentration inside the CC (at the 170th minute of the experiment) indicate that the explosion took place in the inner space of the CC.

Table 1 presents numerical data for this experiment. These data could be presented and analyzed graphically, for example, in the form of I-C and T-C plots (see [2]).

Table1. Experimental data used for making I-C and T-C plots

I_{air} l/min	I_{hy} l/min	C_{hy} % v/v	C_{stat} % v/v	I_{cat} g/h	T(lower) ^0C	T (middle) ^0C	T(upper) ^0C	T(gas) ^0C
21.8	0	0	0	0	25	25	25	25
21.8	1.6	6.84	2.03	6.26	95	114	134	45
21.8	2.1	8.79	3.6	7.07	160	195	195	60
21.8	2.4	9.92	4.41	7.72	195	232	217	66
21.8	3.0	12.1	5.8	9.23	250	279	240	70
21.8	3.65	14.4	6.82	11.50	292	313	250	75
21.8	4.25	16.31	7.9	13.61	328	340	258	80
21.8	4.7	17.74	9.1	14.31	360	364	265	80
21.8	5.6	20.4	10.65	17.23	383	391	272	80
21.8	6.45	22.66	11.75	20.52	395	410	270	80
21.8	7.42	25.36	14.08	22.63	390	425	280	85
21.8	7.72	26.15	14.35	23.98	390	430	280	85

It is important to note the link between the flow of hydrogen entering the CC and the rate of its removal through the catalytic reaction. In our experience, the value of I_{hy}/I_{cat} should lie between 1.2 and 1.8. In the experiment described above, the value of I_{hy}/I_{cat} was maintained between 1.3 and 1.7. Exceeding these limits for I_{hy}/I_{cat} leads to a lower achievable concentration of hydrogen or lower accuracy of measurements in the experiment.

CONCLUSIONS

A climatic chamber was developed and used for safe testing of and research into catalysts for hydrogen-oxygen recombination in an atmosphere containing high concentrations of hydrogen (up to 20 % v/v).

A new "gas stream method" was proposed for studying the kinetics and temperature regime of the working catalyst for hydrogen-oxygen recombination under conditions of natural convection and constant flow of gas through the climatic chamber.

Practical features and safety measures for the experiments, which carry a risk of hydrogen ignition inside the climatic chamber, were described.

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