Performance tests of catalysts for the safe conversion of hydrogen inside the nuclear waste containers in Fukushima Daiichi

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Abstract

The safe decommissioning as well as decontamination of the radioactive waste resulting from the nuclear accident in Fukushima Daiichi represents a huge task for the next decade. At present, research and development on long-term safe storage containers has become an urgent task with international cooperation in Japan. One challenge is the generation of hydrogen and oxygen in significant amounts by means of radiolysis inside the containers, as the nuclear waste contains a large portion of sea water. The generation of radiolysis gases may lead to a significant pressure build-up inside the containers and to the formation of flammable gases with the risk of ignition and the loss of integrity.

In the framework of the project “R&D on technology for reducing concentration of flammable gases generated in long-term waste storage containers” funded by the Japanese Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT), the potential application of catalytic recombiner devices inside the storage containers is investigated. In this context, a suitable catalyst based on the so-called intelligent automotive catalyst for use in a recombiner is under consideration. The catalyst is originally developed and mass-produced for automotive exhaust gas purification, and is characterized by having a self-healing function of precious metals (Pd, Pt and Rh) dissolved as a solid solution in the perovskite type oxides. The basic features of this catalyst have been tested in an experimental program. The test series in the REKO-4 facility has revealed the basic characteristics of the catalyst required for designing the recombiner system.

1 Introduction

In 2011, the Fukushima Daiichi nuclear power plant lost off-site and on-site external power supply as a consequence of the giant tsunami. Subsequently, the chemical reaction of hot steam with the zirconium alloy cladding of the fuel rods generated large amounts of hydrogen gas inside the reactor pressure vessel. Hydrogen leaking from the primary containment into the reactor building led to the formation of flammable gas mixtures followed by hydrogen explosions in several reactor units [1].

The safe decommissioning as well as decontamination of the radioactive waste resulting from the nuclear accident represents a huge task for the next decade. Again, hydrogen represents a safety risk

for the long-term storage of highly radioactive materials. As the nuclear waste contains a significant amount of sea water, the production of radiolysis gases hydrogen and oxygen may result in a pressure build-up inside the containers with the risk of the formation of flammable gas mixtures.

Since the Fukushima Daiichi accident, the request of hydrogen mitigation technologies has significantly increased especially in Asian countries. Meanwhile, passive autocatalytic recombiners (PAR) have been implemented in nuclear power plants worldwide [2] and are consequently considered for application inside the nuclear waste storage containers (Fig. 1). The main feature of a PAR is the exothermal reaction of hydrogen and oxygen on the catalytic surfaces even outside the conventional flammability limits. As the heat of reaction creates a buoyancy-driven flow, PARs are considered as entirely passive safety devices without the need of external power supply [3,4].

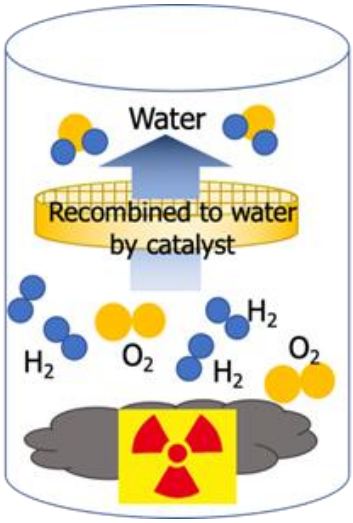

Figure 1. The concept of passive auto-catalytic recombiners (PAR) inside nuclear waste containers

In the framework of the project “R&D on technology for reducing concentration of flammable gases generated in long-term waste storage containers” funded by the Japanese Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT), the potential application of catalytic recombiner devices inside the nuclear waste storage containers is under investigation. In this context, the monolithic “intelligent catalyst” which is currently installed in automobiles is under consideration, as it has shown great suitability for the application in PARs [5-8]. In order to acquire the knowledge for designing the catalyst and the container that is suitable for the long-term storage of highly radioactive materials, basic operational characteristics of the catalyst as a function of the cell density, the catalyst thickness and the chimney height were investigated.

2 Catalyst preparation and characterization

An “intelligent catalyst” is the nanostructure designed perovskite catalyst for automotive emissions control, which has the rejuvenating function instead of preventing aging [6-8]. Catalytically active precious metal is dissolved in a host perovskite lattice forming solid solutions, and released on the surface as metallic nano-particles according to the inherent redox fluctuation of the exhaust (Fig. 2).

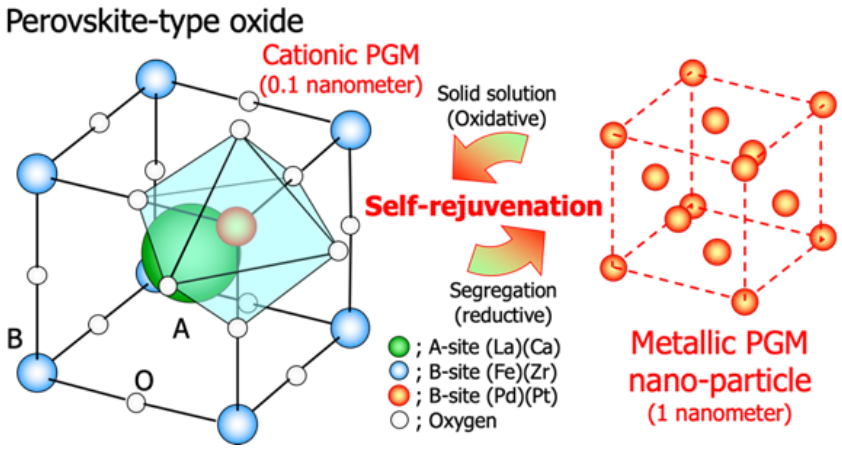

Figure 2. Self-rejuvenation function of the "intelligent catalyst" [7]

The function was actually applied to Pd, Rh and Pt, put to practical use in 2002, and has been adopted for super-ultra-low-emission-vehicles (SULEV) exceeding 6.5 million automobiles. Fig. 3 shows a structure of the "intelligent catalyst" made of ceramics, whose size is 93 mm in diameter and 90 mm in height. Cell density is expressed in 900 cells per square inch (cpsi). The flow channel spacing is about 0.8 mm. Wash-coat is subjected on the ceramic monolithic substrate made of cordierite. The wash-coat contains Pd-perovskite, Rh-perovskite, Pt-perovskite, alumina, ceria, and zirconia. The total amount of precious metal used is as small as about 1.0 g / piece of catalyst. Automobile catalysts are lightweight, have heat resistance up to 1000 °C, and can be considered to be mass-produced technology with a high degree of completion.

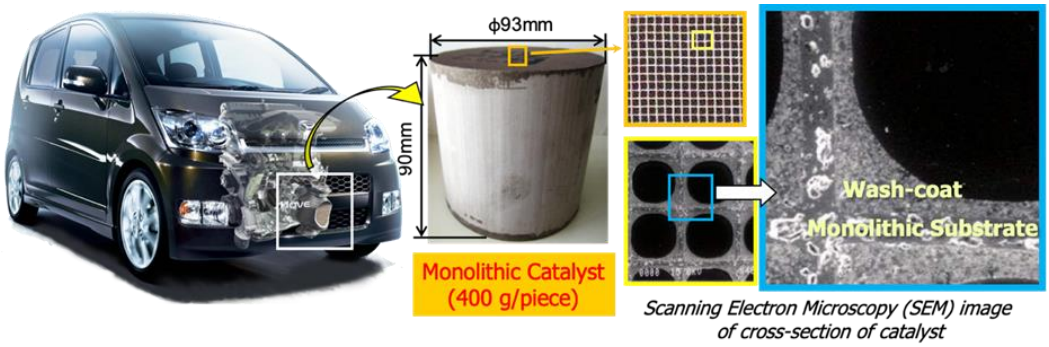

Figure 3. Super-Ultra-Low-Emission-Vehicle with the "intelligent catalyst"

Various kinds of monolith intelligent catalysts which have different cell densities, thicknesses, and diameters were prepared for the application in PAR. The configurations of monolith catalysts are shown in Table 1. The appearances of different cell densities are shown in Fig. 4. Even with the largest diameter of 93 mm and a thickness of 10 mm, the amount of precious metal used is only 0.1 g.

Table 1. The configurations of monolith catalysts.

Number	**Cell density / cpsi**	**Catalyst thickness / mm**	**Diameter / mm**
(i)	30	10	29.4
(ii)	100	10	29.4
(iii)	900	10	29.4
(iv)	30	10	70
(v)	100	10	70

(vi)	900	10	93
(vii)	900	5	93
(viii)	30	3.5	93
(ix)	30	5	93
(x)	30	10	93

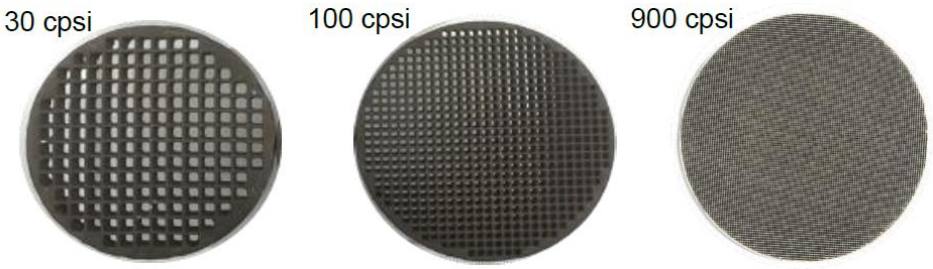

Figure 4. Catalyst specimen with different cell densities

Even if the expected boundary conditions within the container are currently largely unknown, it can be assumed that the temperatures will be well below those for automotive applications. First characterization tests were therefore carried out in order to be able to evaluate the range of application of the catalyst at low temperatures [9]. The schematic picture of the experimental equipment is shown in Fig. 5 (left). In the laboratory scale test apparatus, the monolith catalyst is mounted inside a glass reactor. Catalysts (i) – (iii) with different cell densities (30-900 cpsi) have been used in these tests.

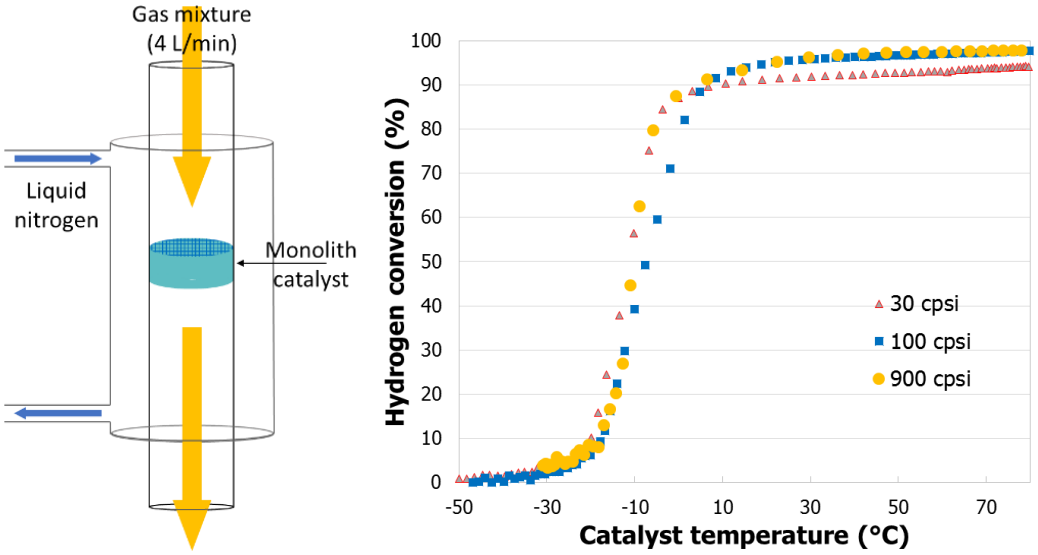

Figure 5. Schematic picture of laboratory scale test apparatus (left), catalyst temperature and hydrogen conversion for different cell densities (right) [9]

The results of the laboratory tests are shown in Fig. 5 (right). Initially, the catalyst is cooled down to a temperature of -50 °C by means of liquid nitrogen. A gaseous mixture (4 vol.% H_2, 10 vol.% O_2, balanced with N_2) is fed into the reactor at a flow rate of 4.0 L/min. Initially, the catalyst temperature increases towards room temperature. Strong temperature increase is then observed due to the start of the hydrogen oxidation reaction on the catalyst surface.

All catalyst samples activate at approx. -20 °C. With increasing temperature, the hydrogen conversion reaches approx. 98 % for the highest cell densities (100 cpsi and 900 cpsi) and approx. 94 % for the lowest cell density (30 cpsi). As the hydrogen oxidation reaction starts well below the freezing point,

the results confirm the general applicability of the monolithic intelligent catalyst for the desired application.

3 Performance tests

The goal of the performance tests was to study the catalyst behavior under natural flow conditions. The test program includes both stationary and dynamic tests.

3.1 Description of REKO-4 test facility

The REKO-4 facility operated at Forschungszentrum Jülich, Germany was designed to investigate the operational behavior of passive auto-catalytic recombiners [10,11]. The facility consists of a cylindrical steel pressure vessel with a free volume of 5.3 m³ (1.4 m diameter, 3.7 m height), including wall heating and outer insulation (Fig. 6). Gases (hydrogen, air, nitrogen) are injected by means of mass flow controllers in radial direction into the vessel at an elevation of approx. 20 cm above the bottom grid. The vessel is equipped with thermocouples for wall and gas temperature measurements. To determine the pressure inside the vessel, relative and absolute pressure sensors are applied. Furthermore, hydrogen, oxygen, and humidity sensors are installed to measure on-line the gas distribution in the course of an experiment. A vertical fan located above the injection line enables the homogenization of the vessel atmosphere.

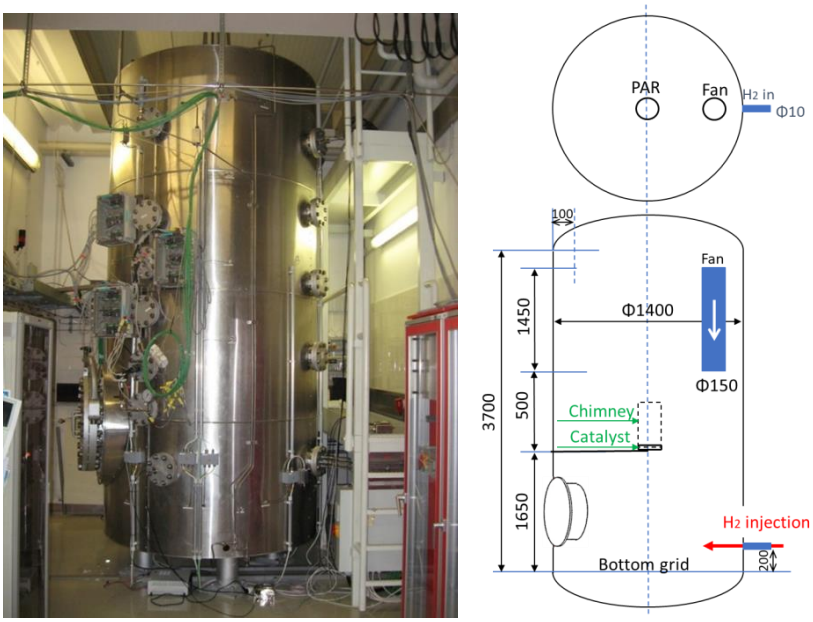

Figure 6. REKO-4 test vessel, photograph (left), schematic (right), dimensions in mm

3.2 Mounting of the catalyst and instrumentation

In the present tests, catalysts with a cell density of 30 cpsi have been used (nbs. (viii), (ix), (x), see Tab. 1). The catalyst specimens are positioned in the center of the pressure vessel at an elevation of approx. 1.65 m. Chimneys of 50 mm and 300 mm in height were prepared. Both are made of stainless steel and have an inner diameter of 100 mm. If the small chimney (50 mm) is used, three catalysts are placed on a coarse stainless steel wire support (Fig. 7, left) in order to enhance the overall recombination rate. The large chimney (300 mm, see Fig. 7, right) has an internal wire support at the bottom end for one single catalyst.

Figure 7. Catalyst samples with small chimneys (left) and large chimney (right)

The instrumentation used for this test campaign includes measurements inside the vessel atmosphere and at the recombiner (Fig. 8). In the vessel atmosphere, temperature (TR) and hydrogen concentration (KR) measurements are located at the bottom (TR 4.19-27, KR 4.02-03+05), middle (TR 4.10-18, KR 4.11-13) and top (TR 4.01-09, KR 4.15-17) levels. Absolute and relative humidity (HR 4.01-02) as well as oxygen concentration (O2R 4.01-02) are measured at the bottom and top levels. PAR instrumentation includes catalyst temperature measurements at the catalyst center (TR 4.90) and rim (TR 4.91), gas temperature measurement at the inlet (TR 4.88), outlet (TR 4.92) and inside the chimney (TR 4.89), as well as hydrogen concentration measurement at the inlet (KR 4.04 + 06) and outlet (KR 4.10).

Gas and catalyst temperatures are measured by means of thermocouples of type K (cromel-alumel, class 2) with a diameter of 1 mm. According to the manufacturer's information and the operating experience, a measurement uncertainty of +/- 0.5 K is expected. Due to the heat radiation effect from the hot catalyst samples, unavoidable higher measurement errors have to be taken into account for the gas temperatures depending on the thermocouple position, especially below the catalyst specimen.

For in-situ measurement of the hydrogen concentration, heat conductivity sensors (Xensor Integration, Type: XEN-TCG3880 + Pt100) are installed. The measurement accuracy under the conditions inside the vessel atmosphere has been checked to be within an absolute value of 0.1 vol.%. However, at the PAR outlet the effect of hot gases passing the sensor affects the sensor signals significantly. For this reason these signals can only serve as qualitative estimates of the hydrogen concentration after the chimney flow has started. Nevertheless, they give accurate information about start-up and termination of PAR operation.

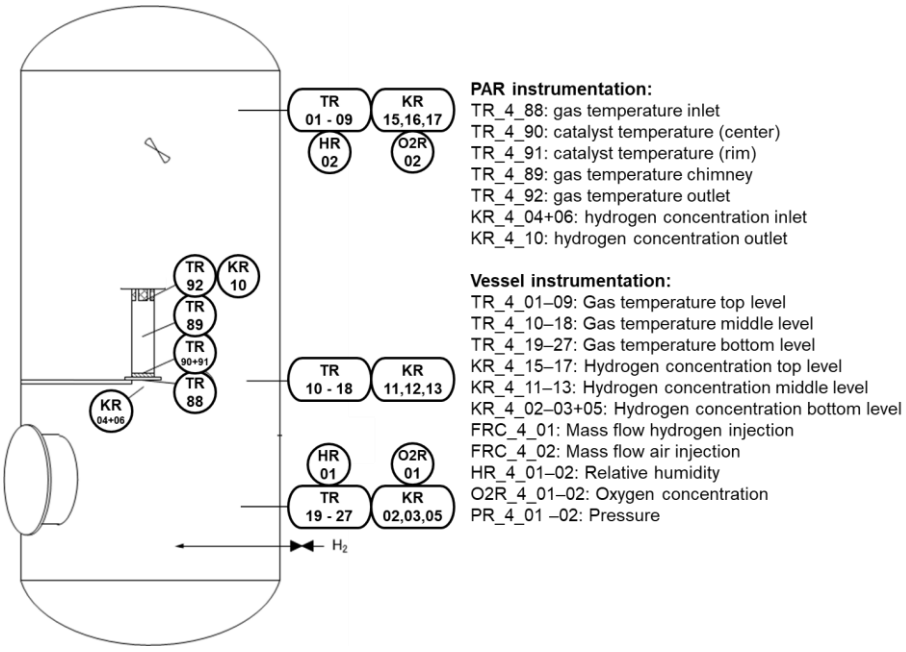

Figure 8. Instrumentation of the test vessel

3.3 Test procedure

The test program includes both stationary and dynamic tests. All tests start in dry air atmosphere at a pressure of 1 bar. The fan is continuously operated in order to obtain well-mixed conditions at all times. The initial vessel temperature is between 20 °C and 35 °C, depending on the corresponding previous test.

For the stationary tests, hydrogen is injected into the vessel at a constant feed rate until the desired hydrogen concentration level (1, 2, 4 and 6 vol.%, respectively) is reached. Then, the feed rate is adjusted in order to reach steady-state conditions. The objectives of these tests are to determine the hydrogen recombination rate and the flow velocity of natural convection. Under steady-state conditions, the recombination rate equals to the injection rate. The flow velocity is then calculated using the conversion efficiencies determined in the laboratory tests.

Figs. 9 and 10 show exemplarily the course of a stationary test. Initially, hydrogen is injected at a feed rate of 0.5 m³/h (Fig. 9, black curve). Due to the fan operation, a homogeneous hydrogen concentration inside the entire vessel is obtained. Sensor KR-4-5 is located underneath the hydrogen injection line. Hence, the signal is fluctuating due to downward-directed fan operation (see also Fig. 6). The start of the hydrogen conversion on the catalyst is indicated by the increase in catalyst temperatures, the increase of the gas temperatures above the catalyst and at the PAR outlet, and the decrease of the hydrogen concentration at the PAR outlet (Fig. 10). After a hydrogen concentration of 2 vol.% is reached inside the vessel, the injection is reduced to 0.1 m³/h (Fig. 9). As the hydrogen concentration remains constant, the hydrogen conversion rate of the catalyst is balanced by the hydrogen feed rate.

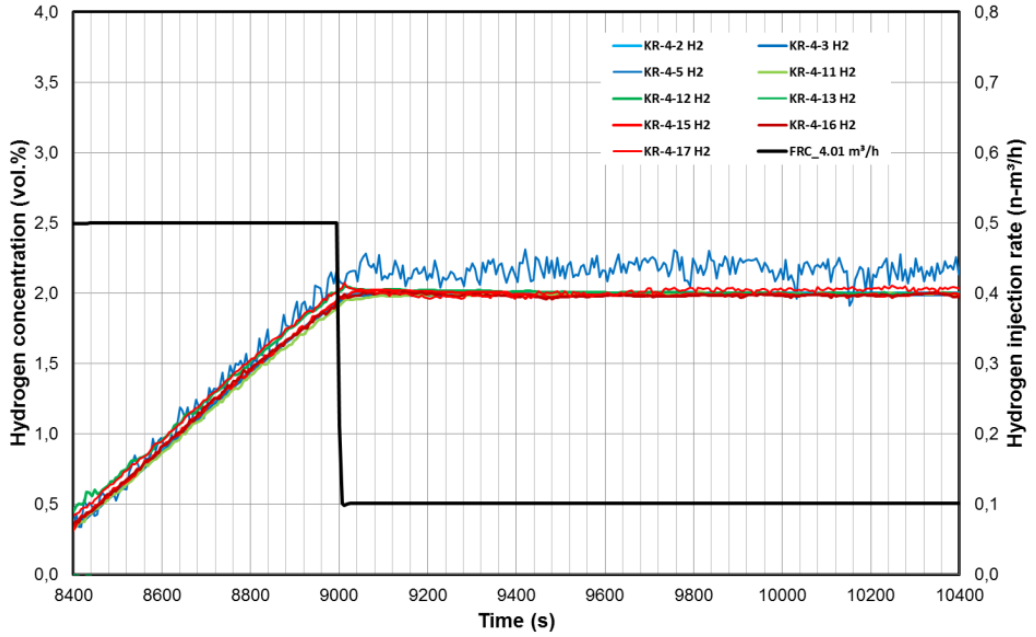

Figure 9. Test procedure of the stationary tests (example): Hydrogen injection rate and concentration inside the vessel

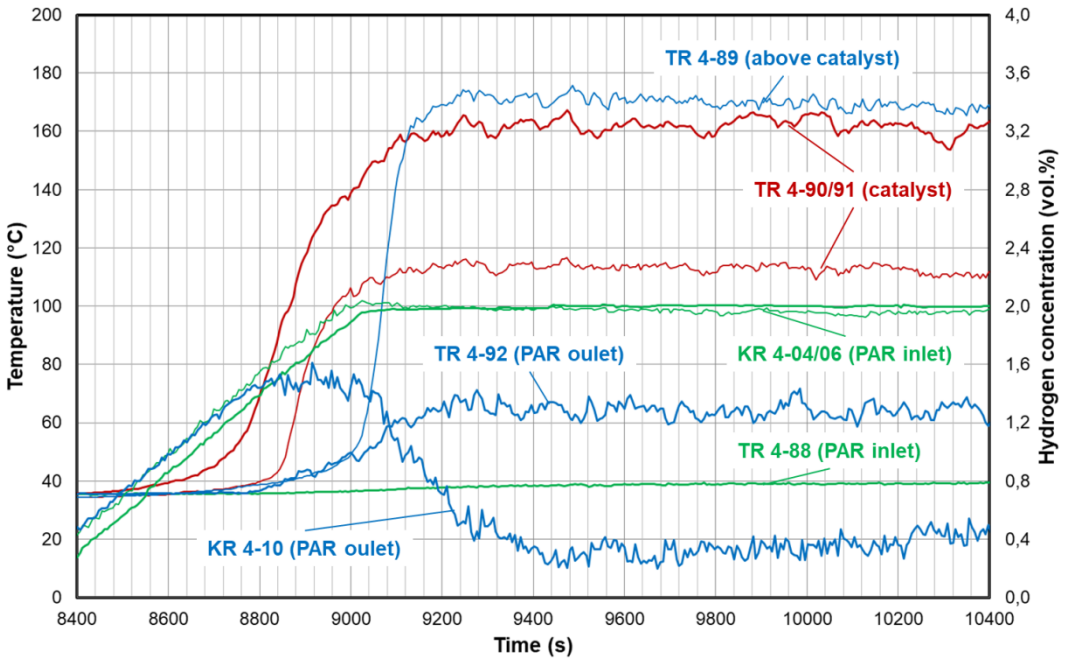

Figure 10. Test procedure of the stationary tests (example): Temperatures and hydrogen concentration at the PAR

For the dynamic tests, hydrogen gas is injected into the vessel to reach the concentration of 6 vol.%. After stop of the injection, the reduction of hydrogen is measured. The objective of these tests is to confirm and assess the hydrogen conversion capability of the corresponding catalyst specimens. Fig. 11 shows exemplarily the decline of the hydrogen concentration after the hydrogen injection has been stopped. The corresponding catalyst temperatures at the center and rim position are given in Fig. 12.

The sharp drop of the temperature at the catalyst center at approx. 15900 s indicates the termination of the catalytic reaction at approx. 0.8 vol.% hydrogen.

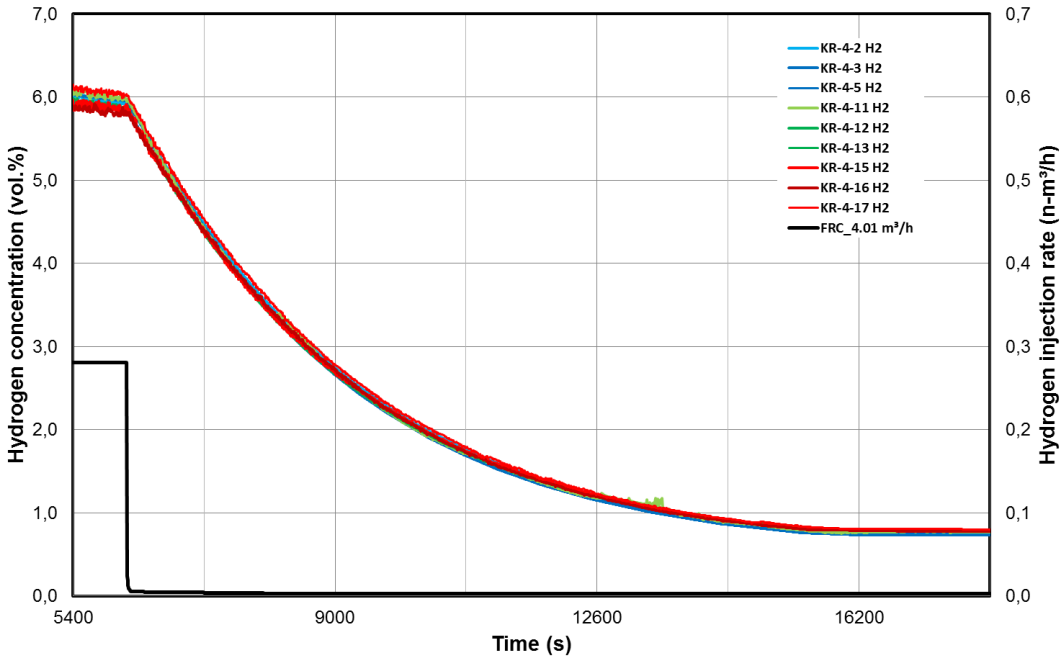

Figure 11. Test procedure of the transient tests (example): Hydrogen concentration inside the vessel

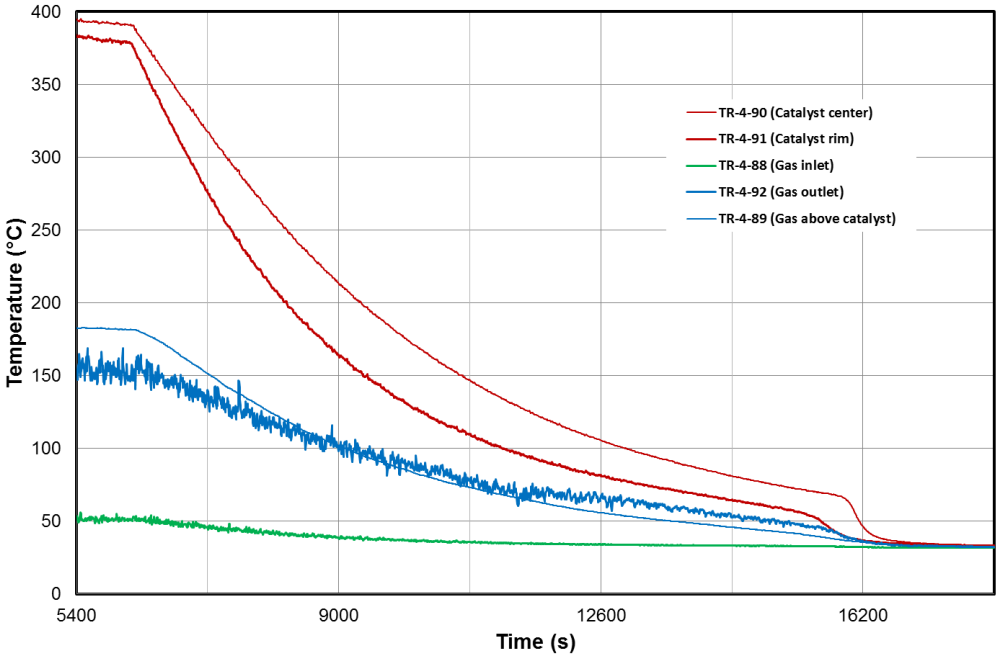

Figure 12. Test procedure of the transient tests (example): Temperatures at the PAR

4 Results

The effect of the chimney height on the recombination rate is shown in Fig. 13. The recombination rates increase linearly with the hydrogen concentration. While the small chimney doesn't contribute

significantly to the hydrogen conversion, the large chimney enables almost three times higher recombination rates compared to the cases without any chimney.

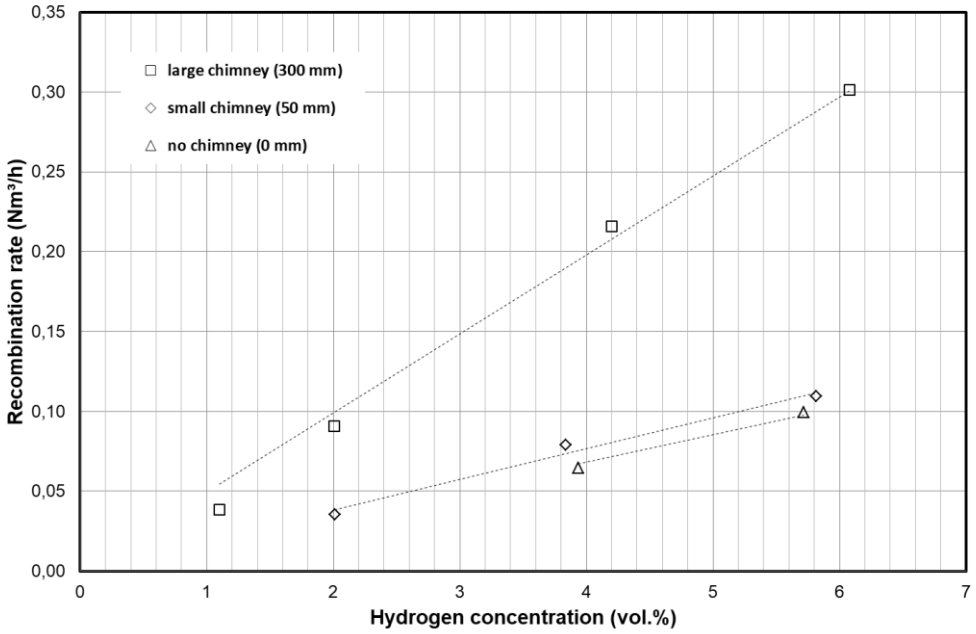

Figure 13. Effect of the chimney height on the recombination rate (catalyst thickness: 5 mm, cell density: 30 cpsi)

While the chimney length has a strong impact on the recombination rate, the effect of the catalyst thickness is negligible. In Fig. 14, the recombination rates obtained with different catalysts are plotted against the hydrogen concentration. All tests were performed with the large chimney (300 mm).

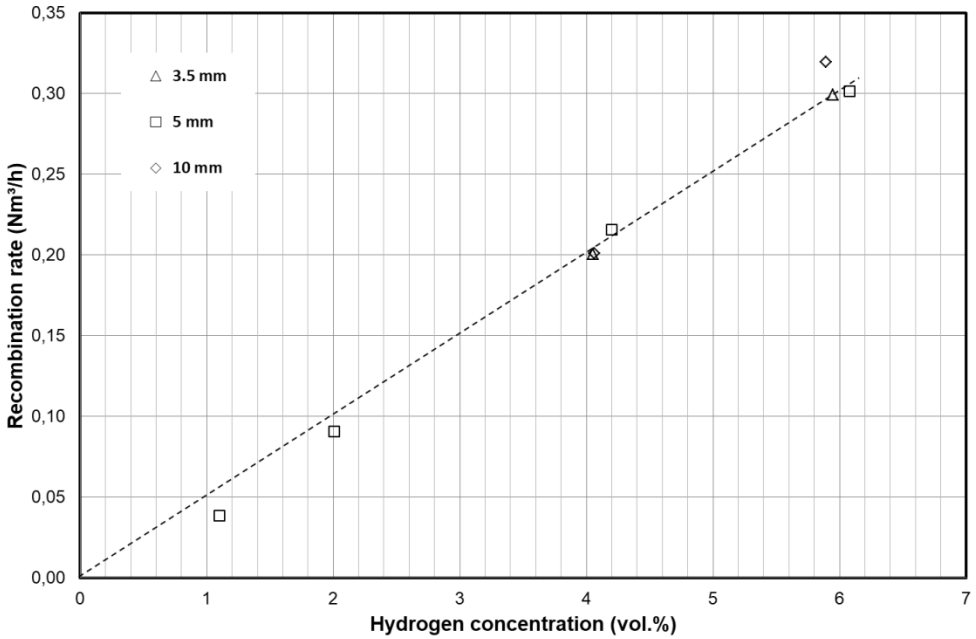

Figure 14. Effect of the catalyst thickness on the recombination rate (cell density: 30 cpsi, large chimney)

Knowing the catalyst efficiency from former tests enables to calculate the flow velocity through the PAR. The supporting effect of the chimney on the flow velocity is illustrated in Fig. 15. Again, the small chimney has only limited effect.

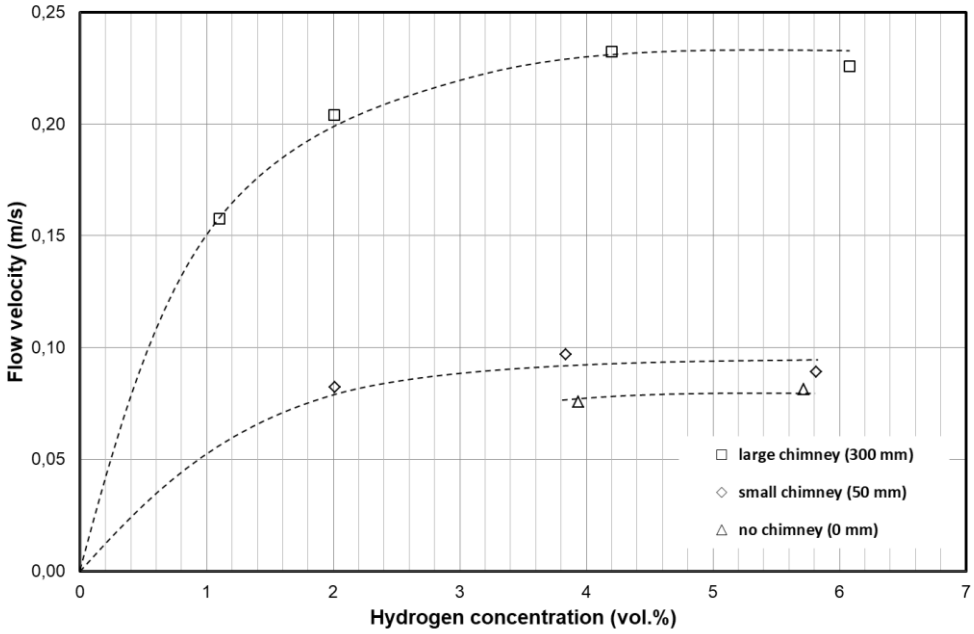

Figure 15. Effect of the chimney height on the flow velocity (catalyst thickness: 5 mm, cell density: 30 cpsi)

Ono et al. [9] compared the present results with former tests results with catalysts of higher cell density in order to study the effect of the cell density on the PAR flow velocity and catalyst temperature (Fig. 16). Under the forced flow tests in laboratory scale, the catalyst with finer cell density showed slightly higher hydrogen oxidation rate, while under natural convection conditions, the catalyst with coarser cell density exhibits significantly higher flow velocities due to reduction of the flow resistance.

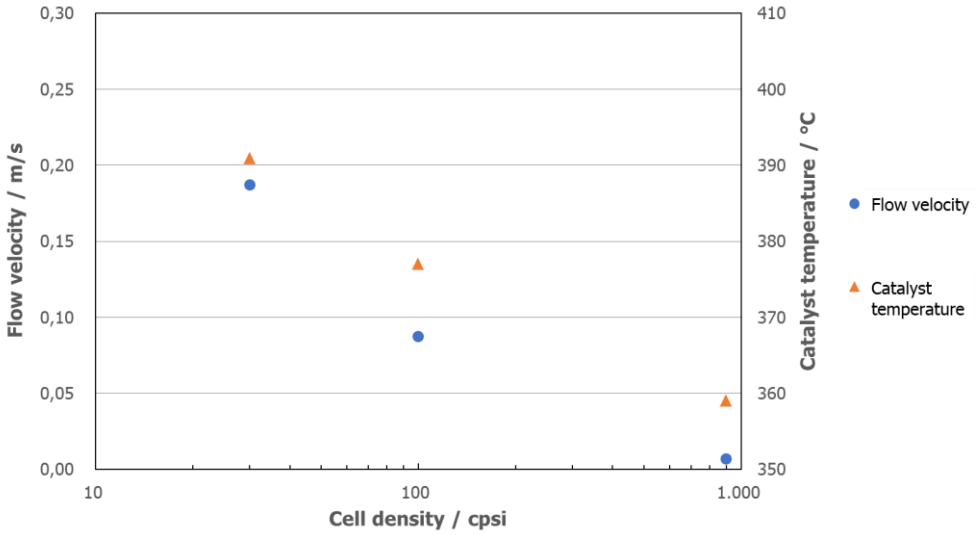

Figure 16. Effect of the cell density on the flow velocity of natural convection and the catalyst temperature (hydrogen concentration: 6 vol.%, catalyst thickness: 5 mm, large chimney) [9]

A comparison of the influence of the catalyst thickness for different cell densities is shown in Fig. 17. With a cell density of 900 cpsi the flow velocity is significantly affected by the catalyst thickness by a factor of 10. Obviously, the significant increase of the pressure loss causes the almost complete stop of the chimney flow. On the other hand, the effect of the catalyst thickness is by far less pronounced when the catalysts with 30 cpsi are used. Here the flow velocities are within a range between 0.217 and 0.239 m/s.

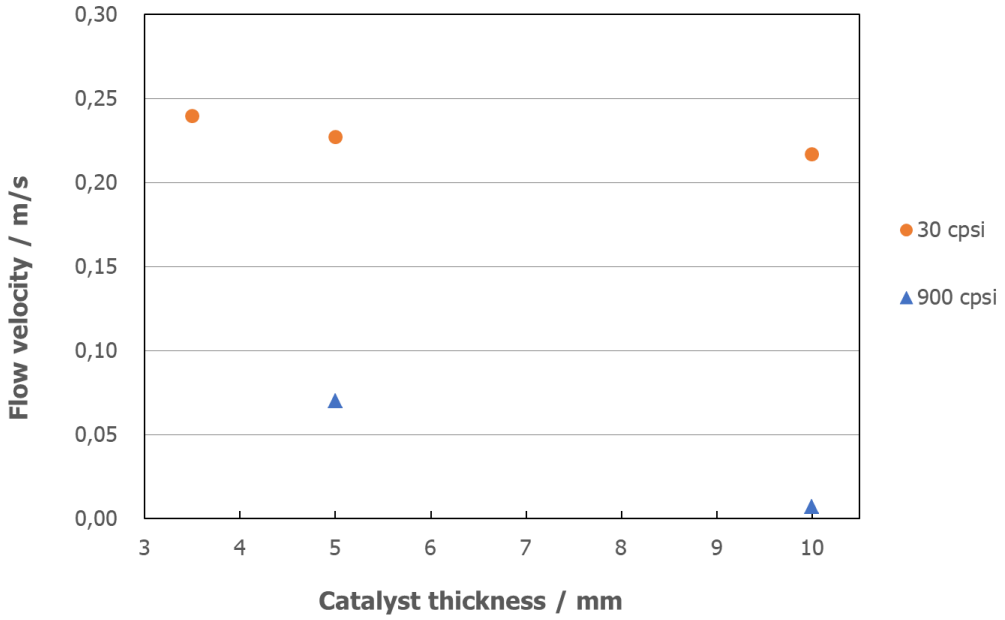

Figure 17. Effect of the catalyst thickness on the flow velocity of natural convection (hydrogen concentration: 6 vol.%, large chimney) [9]

All catalyst set-ups used in the present test series show very similar behavior in the dynamic tests. In all cases, the hydrogen injection is stopped at 6 vol.% and the depleting process is observed until the recombination process stops (see Figs. 11 and 12). The 3 catalysts without any chimney obtain similar residual hydrogen concentrations between 0.6 – 0.8 vol.% as the single catalysts in the large chimney (Fig. 18). Furthermore, all these set-ups need a similar time between 161 and 165 min to obtain these concentration values. For unknown reasons, the 3 catalysts using the small chimneys stop operation already at 1.12 vol.% hydrogen. The analysis of the test conditions, e.g. humidity or oxygen concentration, couldn't give any indication for this unexpected behavior.

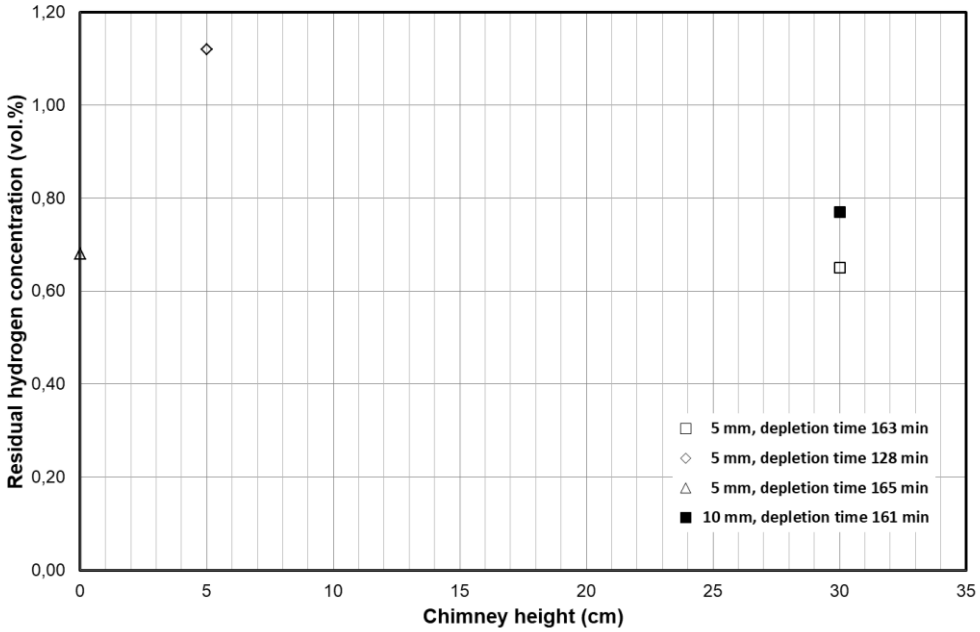

Figure 18. Residual hydrogen concentration obtained for different catalyst set-ups

5 Summary and conclusions

In the framework of the project "R&D on technology for reducing concentration of flammable gases generated in long-term waste storage containers" funded by the Japanese Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT), the potential application of catalytic recombiner devices inside nuclear waste storage containers is investigated. In this context, the monolithic "intelligent catalyst" which is currently installed in automobiles is under consideration. In order to further acquire the knowledge for designing the catalyst, basic operational characteristics as a function of the cell density, the catalyst thickness and the chimney height were investigated.

In test series at both laboratory and system scale the applicability of the monolithic "intelligent catalyst" to PAR was experimentally confirmed. Under forced flow, the catalyst starts hydrogen conversion from below the freezing point. Hydrogen conversion efficiency increases with the cell density. In natural convection however, the recombination rates can be greatly improved by design optimization from automotive (900 cpsi) to PAR (30 cpsi) as a consequence of flow resistance reduction due to coarse cell density. The natural convection flow velocity increases with the installed chimney height, while there is little relationship between the catalyst thickness and the recombination rate.

In summary, the experimental program has clarified the parameters required for designing the PAR system using the monolithic "intelligent catalyst" for application inside containers for long-term storage of high-concentration radioactive waste in Fukushima Daiichi.

Acknowledgements

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