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 PAR system.

1.0 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). Main feature is the exothermal
reaction of hydrogen and oxygen on the catalytic surfaces even outside conventional flammability limits. As the reaction heat creates a buoyancy-driven flow, PARs are considered as entirely passive safety devices without the need of external power supply [3,4].

![Diagram of passive auto-catalytic recombiners (PAR) inside nuclear waste containers](image)

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 investigated. 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.

### 2.0 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).

![Diagram of perovskite-type oxide](image)

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 density and thickness were prepared for 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.

<table>
<thead>
<tr>
<th>Number</th>
<th>Cell density / cpsi</th>
<th>Catalyst thickness / mm</th>
<th>Diameter / mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>30</td>
<td>10</td>
<td>29.4</td>
</tr>
<tr>
<td>(ii)</td>
<td>100</td>
<td>10</td>
<td>29.4</td>
</tr>
<tr>
<td>(iii)</td>
<td>900</td>
<td>10</td>
<td>29.4</td>
</tr>
<tr>
<td>(iv)</td>
<td>30</td>
<td>10</td>
<td>70</td>
</tr>
<tr>
<td>(v)</td>
<td>100</td>
<td>10</td>
<td>70</td>
</tr>
<tr>
<td>(vi)</td>
<td>900</td>
<td>10</td>
<td>93</td>
</tr>
<tr>
<td>(vii)</td>
<td>900</td>
<td>5</td>
<td>93</td>
</tr>
<tr>
<td>(viii)</td>
<td>30</td>
<td>3.5</td>
<td>93</td>
</tr>
<tr>
<td>(ix)</td>
<td>30</td>
<td>5</td>
<td>93</td>
</tr>
<tr>
<td>(x)</td>
<td>30</td>
<td>10</td>
<td>93</td>
</tr>
</tbody>
</table>

Figure 4. Catalyst specimen with different cell densities
The schematic picture of the experimental equipment for first characterization 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.

![Schematic picture of laboratory scale test apparatus](image)

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

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.% H₂, 10 vol.% O₂, balance N₂) 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.

### 3.0 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 [9,10]. 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 in radial direction into the vessel at an elevation of approx. 20 cm above the bottom grid by means of mass flow controllers. 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 enables the homogenization of the vessel atmosphere. Particle Image Velocimetry (PIV) is used to determine the gas flow field at the PAR inlet [10]. The latter option wasn’t made use of in the present investigation.
3.2 Mounting of the catalyst and instrumentation

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 is used, the catalysts are placed on a coarse stainless steel wire support (Fig. 7).

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 4.01-03+05), middle (TR 4.10-18, KR 4.11-12) and top (TR 4.01-09, KR 4.15-17) level. Absolute and relative humidity (HR 4.01-02) as well as oxygen concentration (O2R 4.01-02) are measured at bottom and top level. PAR instrumentation includes catalyst temperature measurement 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).
3.3 Test procedure

The test program includes both stationary and dynamic tests. 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 objective of this test is to determine the hydrogen recombination rate and the flow rate of natural convection. Under steady-state conditions, the recombination rate equals to the injection rate. The flow rate is calculated using the conversion efficiencies determined in the laboratory tests.

Fig. 9 shows exemplarily the course of a stationary test. Initially, hydrogen is injected at a feed rate of 0.5 m³/h (black curve). After an average hydrogen concentration of 2 vol.% is reached inside the vessel, the injection is reduced to 0.1 m³/h. As the hydrogen concentration remains constant, the feed rate corresponds to the hydrogen conversion rate of the catalyst.
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. 10 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. 11. 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 10. Test procedure of the transient tests (example): hydrogen concentrations

Figure 11. Test procedure of the transient tests (example): temperatures
4.0 RESULTS

4.1 Stationary tests

The effect of the cell density on the PAR flow rate and catalyst temperature is shown in Fig. 12. When the catalysts (iv), (v) and (vi) were used, the calculated flow rates are calculated to be 0.187, 0.0873 and 0.007 m/s, respectively. 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 rates due to reduction of the flow resistance.

Figure 12. Effect of cell density on flow rate of natural convection and the catalyst temperature (catalyst thickness: 10 mm, large chimney)

A comparison of the influence of the catalyst thickness is shown in Fig. 13. When the catalysts (vi) and (vii) with 900 cpsi are used, the flow rate is significantly affected by the catalyst thickness by a factor of 10. On the other hand, the effect of the catalyst thickness is by far less pronounced when the catalysts with 30 cpsi (viii), (ix) and (x) are used. The flow rates obtained range between 0.239 and 0.217 m/s.

Figure 13. Effect of catalyst thickness on the flow rate of natural convection (large chimney)
The effect of different chimney heights is shown in Fig. 14. In contrast to the chimney height, the hydrogen concentration level is of secondary relevance for the flow rate. Using the 300 mm chimney, the flow rate is increased by a factor of approx. 2.5 compared to the small chimney.

![Graph showing flow rate vs. chimney height](image1)

Figure 14. Effect of chimney height on flow rate of natural convection
(catalyst thickness: 10 mm, cell density: 30 cpsi)

### 4.2 Dynamic tests

The findings of the stationary tests are also reflected in the dynamic tests results. Figs. 15 and 16 show the hydrogen depletion curves for catalyst specimens (vii) and (ix), respectively. For catalyst (vii) with a cell density of 900 cpsi it takes approx. 12 hours to reduce the hydrogen concentration from 6 vol.% down to 1.5 vol.%. In contrast, it takes just approx. 3 hours to reduce the hydrogen concentration down to 0.6 vol.% for catalyst (ix) with a cell density of 30 cpsi. By using the catalyst with the coarse cell density, both the recombination rate and the ultimate concentration were significantly improved.

![Graph showing hydrogen depletion during dynamic test](image2)

Figure 15. Hydrogen depletion during the dynamic test (900 cpsi)
5.0 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 flow rate 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 rate increases with the installed chimney height, while there is little relationship between the hydrogen concentration and the flow 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.

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REFERENCES


