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A proposal of hydrogen safety technology for decommissioning of the Fukushima Daiichi Nuclear Power Station

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ABSTRACT

The safe removal, transportation, and long-term storage of fuel debris in the decommissioning of Fukushima Daiichi is the biggest challenge facing Japan. In the nuclear power field, passive autocatalytic recombiners (PARs) have become established as a technology to prevent hydrogen explosions inside the containment vessel. To utilize PAR as a measure to reduce the concentration of hydrogen generated in the fuel debris storage canister, which is currently an issue, it is required to perform in a sealed environment with high doses of radiation, low temperature, and high humidity, and there are many challenges different from conventional PAR. A honeycomb-shaped catalyst based on automotive catalyst technology has been newly designed as a PAR, and research has been conducted to solve unique problems such as high dose radiation, low temperature, high humidity, coexistence of hydrogen and low oxygen, and catalyst poisons. This paper summarizes the challenges of hydrogen generation in a sealed container, the results of research, and a guide to how to use the PAR for fuel debris storage canisters.

1. Introduction

First of all, the authors would like to take this opportunity to express their sincere gratitude for the tremendous supports and heartwarming messages sent from all over the world immediately after the Great East Japan Earthquake that occurred in March 2011. The earthquake and subsequent tsunami caused insufficient reactor cooling at the Fukushima Daiichi Nuclear Power Station (1F), resulting in a catastrophe including hydrogen explosions and the release of radioactivity into the environment [1–6]. Since then, Japan has continued to address post-disaster treatment as a national issue, such as decontaminating radioactive waste and preventing the spread of contaminated water.

As of today, the major remaining issues are the post-processing of contaminated water and highly radioactive fuel debris [7]. Multiple radionuclides are removed from the contaminated water by Advanced Liquid Processing System (ALPS) [8], but water containing tritium has been treated and released into the ocean since August 2023. This contaminated water is constantly being generated when rainwater and groundwater come into contact with the fuel debris remaining at the bottom of the reactor where the accident occurred. The only fundamental solution is to remove the fuel debris from the reactor. The estimated amount of approximately 880 tons of fuel debris existing at Fukushima Daiichi has been announced to be divided into 70–100 kg portions, to be sealed in about 10,000 fuel debris storage canisters, and to be stored on the site of the Fukushima Daiichi Nuclear Power Station for 30–50 years [9].

A major issue here is that the high dose of radiation contained in the fuel debris causes the water to decompose, generating hydrogen (H_2) and oxygen (O_2) inside the storage canister. According to calculations by Tokyo Electric Power Company Holdings, Inc. (TEPCO), the maximum amount of hydrogen generated within the canister is estimated to be 1.1 $L\ h^{-1}$.

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2. Decommissioning projects for Fukushima Daiichi

At the time of the earthquake, Units 1 to 3 of the Fukushima Daiichi Nuclear Power Station were in operation, and fuel was stored in the reactor cores. The emergency power supply was lost due to the tsunami that followed the earthquake, making it impossible to cool the reactor cores, and the fuel overheated and melted. This cooled, solidified, molten nuclear fuel is called “fuel debris."

On the other hand, “contaminated water” is water that contains high concentrations of radioactive materials. In Units 1 to 3, not only the fuel debris cooling water but also the groundwater and rainwater that flows into the damaged Reactor Pressure Vessel (RPV) and the Primary Containment Vessel (PCV) are exposed to high concentrations of radioactive materials, and “contaminated water” continues to be generated even now. The “contaminated water” is being treated/purified to reduce the concentrations of radioactive substances using multiple types of equipment such as Advanced Liquid Processing System (ALPS). After risks have been sufficiently reduced in this manner, it is stored in tanks on 1F site as “treated water”. However, it is also true that “treated water” has exceeded the capacity of the storage tanks and has already begun to be diluted and discharged into the sea from August 2023 [10,11]. In order to prevent any further “contaminated water” from being produced, it is essential to remove the fuel debris from the reactor that suffered the accident. Removing fuel debris is currently the biggest challenge Japan is facing in decommissioning.

2.1. National projects of decommissioning and contaminated water management

R&D on retrieval, transportation, and long-term storage of radioactive fuel debris has been undertaken by the International Research Institute for Nuclear Decommissioning (IRID) with the support of the Agency for Natural Resources and Energy (ANRE), in the Ministry of Economy, Trade and Industry, of the Japanese government as part of “the decommissioning and contaminated water control project” since 2014 [12,13]. Due to circumstances such as “the radiation dose at the site being relatively low and early access to the inside of the reactor containment vessel being possible,” Unit 2 has been positioned as the first unit for fuel debris removal, and work has been proceeding. However, they are facing numerous obstacles related to high radiation levels, and test sampling of approximately 3 g of fuel debris, which was originally scheduled to begin in 2021, has been delayed by more than three years.

Approximately 880 tons of fuel debris existing at Fukushima Daiichi will be removed from the reactor, and divided into 70–100 kg portions, packed into storage canisters, and transported to a storage area on the site. Plans have been announced to store as many as 10,000 fuel debris storage canisters for a long period of 30–50 years on the site, and then transport them to final processing facilities. A major issue here is that the high dose of radiation contained in the fuel debris causes the water to decompose, generating H_2 and O_2 inside the storage canister. This national project has set the management standard value for H_2 concentration inside the storage canister at 4.0% or less by volume, and is exploring promising methods to reduce it. IRID has also presented ideas such as drying the fuel debris in advance and fully opening the ventilation valve of the storage canister, and the technical policy is updated each time decommissioning technology development progresses. Thus, the fuel debris removal work in the decommissioning project at Fukushima Daiichi is understood to be a difficult challenge never before experienced by mankind.

2.2. Hydrogen generation in fuel debris canisters

In the governmental decommissioning project, it is reported that fuel debris will be packed in a mesh unit canister and then stacked in two layers in a storage canister for transportation and long-term storage. It is also reported that the inner diameter of the fuel debris storage canister should be as small as 220 mm to maintain sub-criticality. On the other hand, there are no particular restrictions on the height, with the internal dimension reported to be 840 mm, so the internal volume is about 32 L (Fig. 1) [13]. The packed bed of the catalyst is considered to have a diameter of 200 mm and a height of about 10 mm (314 cm^3). It is also equipped with ventilation, and the inner diameter of the coupler is reported to be 25.4 mm. Approximately 880 tons of fuel debris will be divided into canisters of 70–100 kg each and transported to a storage area on the site. Up to 10,000 fuel debris canisters will be stored on the site for a long period of time, from 30 to 50 years.

The major issue here is that the high dose of radiation contained in the fuel debris will cause the water to decompose, generating H_2 and O_2 inside the storage canister. According to an estimate by Tokyo Electric Power Company Holdings (TEPCO), the amount of hydrogen generated inside one storage canister is a maximum of 0.011 L h^{-1} per 1 kg of fuel debris. When100 kg of fuel debris is filled in one storage canister, a maximum of 1.1 L h^{-1} of H_2 and 0.55 L h^{-1} of O_2 will be generated, the density of the fuel debris is estimated to be about 6.0 g cm^3, the filled volume will be 16.7 L (volume ratio 62%), the void in the canister will be 15.3 L (volume ratio 48%), and it is calculated that it will take 39 min for the H_2 concentration to exceed the control value of 4%. In order to remove moisture by pre-drying the fuel debris to reduce the H_2 concentration to 4% or less, the calculated moisture content in 100 kg of fuel debris will be 0.49g (water content 4.9 ppm) or less.

Similarly, when one storage canister is filled with 70 kg of fuel debris, a maximum of 0.77 L h^{-1} of hydrogen and 0.385 L h^{-1} of oxygen will be generated, the fuel debris volume will be 11.7 L (volume ratio 36%), the void space in the canister will be 20.3 L (volume ratio 64%), and it is calculated that it will take 68 min for the H_2 concentration to exceed the control value of 4% by volume. Pre-drying of the fuel debris requires that the moisture content in 70 kg of fuel debris be kept below 0.65 g (9.3 ppm in debris), which is a large deviation from the drying target value of 0.1% set by the national project.

When storing the fuel debris for a long period of time in the facility, it is expected that various hydrogen explosion prevention measures will be taken throughout the building. However, the fuel debris must be transported from the reactor building to the storage site on open roads,

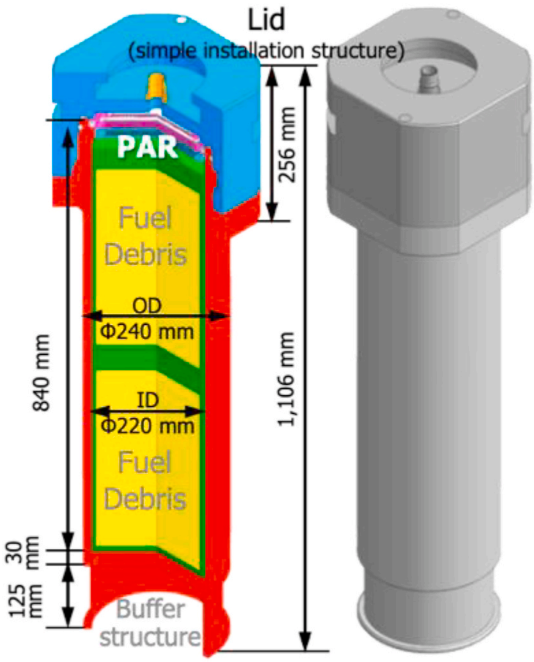


Fig. 1. Fuel debris storage canister design [13]. Dimensions and annotations added to IRID publications.

which is expected to take 7 days. At least 130 L of hydrogen will be generated per fuel debris canister, so technology that can reduce the hydrogen concentration inside the canister is essential. There is a strong demand for the development of technology that can prevent both hydrogen explosions and the dispersion of radioactive materials during the transportation of as many as 10,000 fuel debris canisters.

2.3. *Voluntary international collaborative research on passive autocatalytic recombiner (PAR)*

“No matter how small the scale, a hydrogen explosion must never happen again at Fukushima.” With this pledge in mind, immediately after the accident in 2011, researchers from across the boundaries of industry, government, academia, and both Japan and overseas, including the Japan Atomic Energy Agency, Daihatsu Motor, Kwansei Gakuin University, and Germany’s Jülich Research Center, have come together voluntarily to develop technology to prevent hydrogen explosions. The research has been carried out with independent research funding, separate from any large-scale national projects.

The research group has been working collaboratively on the research and development of catalysts for controlling automotive emissions, and has achieved significant practical results, including the mass production of the “Intelligent Catalysts” [14–18]. In particular, catalyst development based on fundamental scientific analysis using the SPring-8 synchrotron radiation facility has attracted attention [19–22]. This time, contrary to previous projects, the motivation of this independent research group is to use the catalyst technology they developed to improve nuclear safety. In this way, the authors hope to contribute to nuclear safety and the reconstruction of Fukushima from a different perspective than national projects.

One promising countermeasure that can prevent hydrogen explosions and confine radioactive materials at the same time is the “Passive Autocatalytic Recombiner (PAR)." PAR prevents explosions by converting generated H_2 and O_2 back into water through a catalytic reaction. PAR was originally developed to remove hydrogen from containment vessels and prevent hydrogen explosions in the event of a severe accident at a nuclear power plant [23–27]. The recombiner is called a ‘passive’ and ‘autocatalytic’ because it activates spontaneously as soon as H_2 concentrations rise and does not require external energy to operate. It is called a ‘recombiner’ because H_2 and O_2 will be ‘recombined’ to form water (H_2O).

There are records that the use of PAR was previously considered in the decommissioning of the Three Mile Island Nuclear Power Plant Unit 2 (TMI-2) in Pennsylvania, USA [28]. When PAR is used in a sealed closed container such as a fuel debris canister, it is required to have unique characteristics such as long-term high-dose radiation resistance and the ability to operate in low temperature and high humidity environments. It has already been reported that honeycomb-type precious metal catalysts used in automobile catalysts can maintain high activity in low-temperature, high-humidity environments even after exposure to high doses of radiation [29]. In order to reduce the H_2 concentration in a long tall cylinder such as the fuel debris canister in this study, it is particularly important to use the heat generated by the hydrogen oxidation reaction to create a flow of gas passing through the catalyst by natural convection [30–32]. This paper aims to provide an overview of 14 years of collaborative research on the safety of hydrogen generated in enclosed spaces and sealed canisters, and to provide a comprehensive guideline on the advantages and limitations of PAR, as well as how to use it effectively.

3. Experimental

The experimental program was performed in the REKO-T catalytic reactor at Kwansei Gakuin University, Japan and in the REKO-4 facility at Research Center Juelich, Germany, accompanying CFD simulations in order to visualize the hydrogen distribution and flow field inside the fuel debris canister were performed using Ansys Fluent.

3.1. *Prototype of a real-scale visualized transparent storage canister*

A visualized transparent catalytic reactor, with an inner diameter of 230 mm and a height of 840 mm, was prototyped to simulate an actual fuel debris storage canister and named REKO-T (Rekombinator-Transparent). Inside REKO-T, four mesh cages with a diameter of 200 mm and a height of 200 mm were installed to simulate unit cans, and 2500 hollow resin spheres with a diameter of 20 mm (625 spheres packed in four layers) to simulate fuel debris were also installed. In addition, four thermal conductivity detector (TCD) type hydrogen sensors (H sensors) for measuring H_2 concentration, three humidity sensors for measuring relative humidity, and the number of K-type thermocouples (TC) for measuring catalyst temperature and gas temperature are increased as needed. Two types of lids were prepared: one with a hole in the center and a ventilation pipe with an inner diameter of 30 mm and a height of 140 mm, and another without a hole, so that the effect of opening and closing the ventilation pipe could be compared. A catalytic combustion type hydrogen sensor was also equipped directly above the ventilation pipe (Fig. 2).

From the center of the bottom of the visualization reactor REKO-T, N_2 was introduced to carry out nitrogen replacement for 2 h. Then H_2 and O_2 were injected, and the time change in H_2 concentration at each position was measured. As shown in Table 1, the injection amount was increased every hour from Step 1, and in Step 4, 20.0 mL·m-1 of hydrogen, equivalent to the expected maximum hydrogen generation rate of 1.1 L·h-1, and 10.0 mL·m-1 of oxygen were injected at the same time.

3.2. *Monolithic catalyst for REKO-T*

The catalyst used here is an intelligent catalyst for automotive emissions control, with a diameter of 25 mm, height of 10 mm, volume of 4.9 cm^3, and cell of config. #30 (4.4 $cell \cdot cm^{-2}$). Only one piece of the catalyst was used. The amount of precious metals contained in one test piece was Pt:Pd:Rh = 2.45:1.47:1.96 mg. Comparative flow improvement tests were conducted using one catalyst strip cut into two halves and four quarters (Fig. 3).

3.3. *Hydrogen fluid calculation inside fuel debris canister*

In order to visualize the distribution of H_2 concentration and flow rate inside the fuel debris canister, a fluid calculation was performed using the finite element method with Ansys Fluent [33]. The boundary conditions are as follows. The dimensions of the canister were the same as the real fuel debris storage canister, with an inner diameter of 220 mm and an internal height of 840 mm, and an open ventilation pipe with an inner diameter of 25.4 mm and a height of 140 mm was installed in the center of the top. The calculation was performed in an empty storage canister with no obstacles such as fuel debris. H_2 and O_2 were injected at flow rates of 20 $mL\ m^{-1}$ and 10 $mL\ m^{-1}$, respectively, from the center of the bottom of the canister, which was 10 mm in diameter and 30 mm in height, for 0 to 3600 s.

Furthermore, in order to improve the ventilation effect, the change in H_2 concentration distribution when the open ventilation pipe was changed to a thicker and shorter one with an inner diameter of 40 mm and a height of 25 mm was also calculated for 0 to 7200 s.

3.4. *Natural convection and reactivation test using REKO-4*

To investigate the performance in an environment without gas flow, such as a fuel debris canister, experiments were conducted at the Jülich Research Center in Germany. The facility is called REKO-4, and is a reaction vessel with an internal volume of 5450 L. Experiments were conducted by placing three catalysts, each with a diameter of 65 mm and

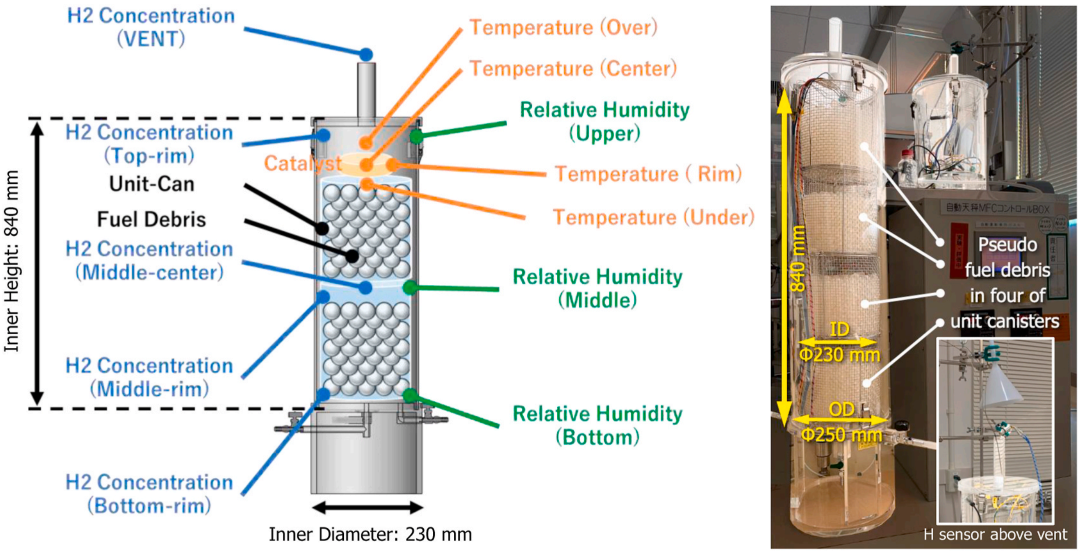


Fig. 2. REKO-T: A visualized transparent catalytic reactor simulating a fuel debris storage canister.

Table 1
Hydrogen oxygen injection schedule.

	Step 1	Step 2	Step 3	Step 4
Time/m	0–60	60–120	120–180	180–240
Injection rate	25%	50%	75%	100%
H_2/mL m^{-1}	5.0	10.0	15.0	20.0
O_2/mL m^{-1}	2.5	5.0	7.5	10.0

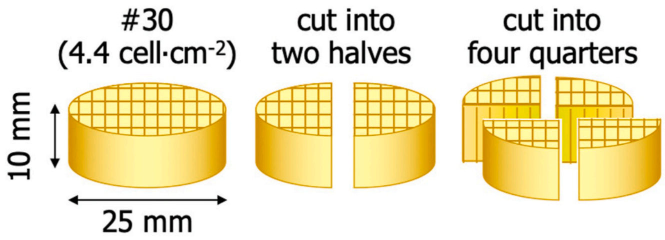


Fig. 3. Intelligent catalysts for REKO-T.

a volume of 33 mL, inside the vessel. The catalyst volume ratio is 1/50,000 of the vessel. The purpose of this experiment is to provide numerical data such as the natural convection velocity and hydrogen conversion amount required for thermal flow analysis by measuring the thermal convection generated by the heat of the catalytic reaction in an environment that is not affected by walls.

The natural convection velocity was measured using honeycomb catalysts with various catalyst materials and configurations. At the beginning of the research, measurements were made using a stainless steel chimney with an inner diameter of 100 mm and a height of 300 mm. Currently, natural convection is created without a chimney by devising the honeycomb configuration.

Furthermore, past experiments have revealed problems with reactivation. After placing a catalyst inside REKO-4 and injecting hydrogen to a concentration of 6% by volume, the reactor was left overnight with all valves closed. The H_2 concentration in the reactor dropped to less than 1.0% by volume, the ambient temperature dropped to room temperature, and the relative humidity reached 100%. Under such low temperature and high humidity conditions, reactivation did not occur even when hydrogen was again injected up to a concentration of 6% by volume.

Previous studies have also shown that the hydrogen oxidation reactivity of PAR used in a closed environment is significantly affected by the cell density of the honeycomb catalyst. Therefore, in this study, various catalysts were fabricated based on the honeycomb support of configuration #30 (4.4 cells·cm^{-2}), including #7 and #3, which were further cut and processed. Here, the honeycomb cell density is conventionally referred to in the automotive industry as “cells per square inch”, and has the structure shown in Table 2.

Pt/Al_2O_3 catalysts, containing 4% platinum by mass relative to the alumina, were prepared by coating on the honeycomb (config. #3) with a diameter of 65 mm and a height of 10 mm. The hydrogen conversion velocity of these Pt/Al_2O_3 catalysts (config. #3) was also measured. Furthermore, catalysts were prepared in which the bottom 2 mm of the 10 mm height of Pt/Al_2O_3 catalysts (config. #3) were immersed in silicone oil (Shin-Etsu Chemical: KF-96), dried and heat-treated to form a water-repellent layer. These two types of Pt/Al_2O_3 (config. #3) catalysts were left overnight in a closed environment with an H_2 concentration of 6% in REKO-4 to recombine the H_2 and O_2, and then reactivation tests were conducted in room temperature, high humidity environment.

4. Results and discussion

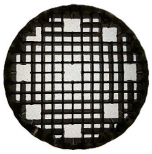
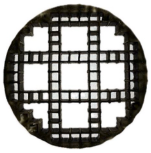
The results of experiments using the REKO-T catalytic reactor, a full-scale visualization of the fuel debris canister, were in good agreement with the results of the CFD simulation. A new challenge, reactivation experiments in a low-temperature, high-humidity environment, was carried out at the REKO-4 facility, and a clue to the solution was found. The details are described below in order.

4.1. Ventilation effect without catalysts

To clarify the effect of the catalyst, the change in H_2 concentration without the catalyst was measured as a baseline with the ventilation fully open, according to the schedule shown in Table 1. The ventilation at the zenith was installed in the hope that the light and highly diffusible H_2 would escape efficiently, but the H_2 concentration continued to rise, so the injection of H_2 and O_2 was stopped 70 min after the start of the test. Furthermore, it was observed that the H_2 concentration did not decrease significantly even 5 h after the H_2 supply was stopped (Fig. 4).

In the experiment, a phenomenon was observed in which the ventilation effect was almost completely eliminated. To verify the validity of the experimental results, a fluid analysis was performed on the change in H_2 concentration inside the fuel debris canister with the ventilation open using the numerical software Ansys Fluent. The H_2

Table 2
Catalyst configurations.

Config. Code	#100	#30	#7	#3
Cell density/cell cm^{-2}	15.5	4.4	1.1	0.5
Cell (hole) size/cm	0.25	0.45	0.91	1.43
Cell configuration	 100 cell inch^{-2}	 30 cell inch^{-2}	 4-Cell holes of #30	 9-Cell holes of #30

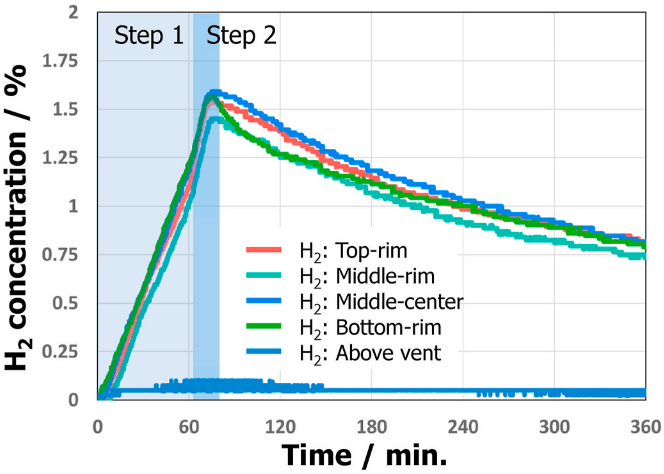


Fig. 4. Hydrogen ventilation effect.

concentrations (molar fractions) after 100 s, 1200 s, 2400 s, and 3600 s are shown (Fig. 5).

What became clear was that hydrogen has good diffusivity, so once it is emitted it forms a uniform mixture inside the canister, and the increased pressure of the total gas mixture is released through the ventilation. Looking inside the ventilation pipe after 3600 s, a steep concentration gradient was observed inside the pipe, which had an inner diameter of 25.4 mm and a length of 140 mm. Next, the ventilation was changed to a wider and shorter diameter of 45 mm and a length of 25 mm, and the results of the same calculation are shown in Fig. 6. An improvement was seen in the H_2 concentration distribution after 3600 s, but after 7200 s it had increased to a concentration of over 0.7%, and it can be seen that the H_2 concentration continues to increase.

4.2. *Hydrogen recombination verification by catalyst arrangement in visualization REKO-T*

The Technical Strategic Plan 2024 (Japanese version) published by the Nuclear Damage Compensation and Decommissioning Facilitation Corporation (NDF) [34] also reiterates the importance of maintaining subcriticality, containment functions, and measures to prevent hydrogen generation in decommissioning the Fukushima Daiichi Nuclear Power Station. To explore the possibility of reducing the H_2 concentration while closing the ventilation in the fuel debris storage canister, the performance and arrangement of the catalyst, a main component of PAR, was examined using REKO-T.

An intelligent catalyst for automobiles with a diameter of 25 mm, height of 10 mm, and cell #30 (4.4 cell cm-2) was used to search for the arrangement that would most efficiently reduce the H_2 concentration in the simulated storage canister. From the center of the bottom of the visualization reactor REKO-T, the amount of H_2 and O_2 injected was increased every hour from Step 1 to 4 as shown in Table 1, and the change in H_2 concentration over time at each position was measured. Please note that in the REKO-T experiment described here, a lid without a ventilation tube was used to verify the possibility of achieving both containment function and hydrogen concentration reduction, and the effect of the catalyst alone was extracted.

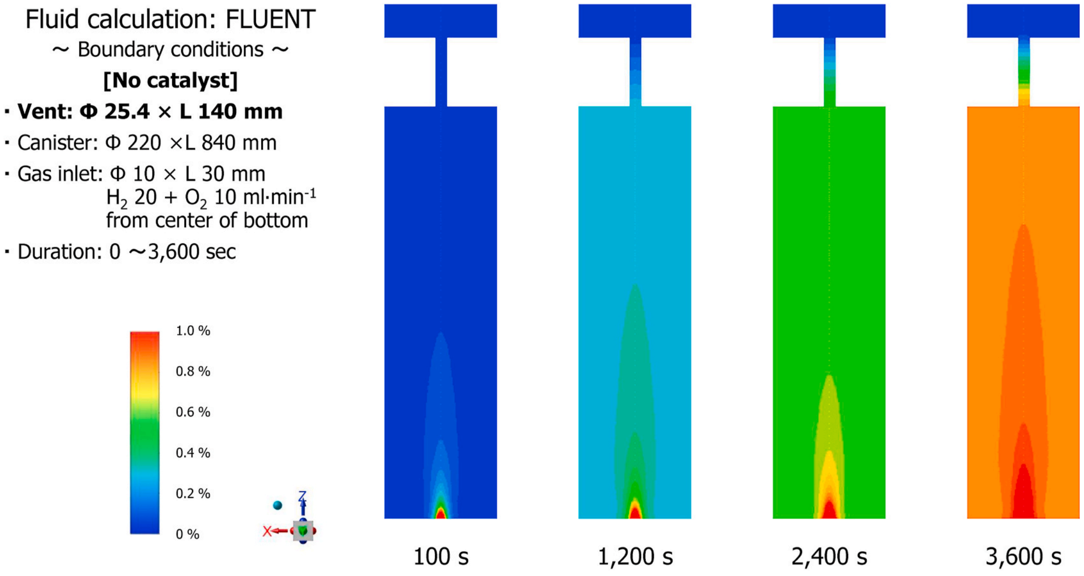


Fig. 5. Fluid analysis on H_2 concentration inside the fuel debris canister.

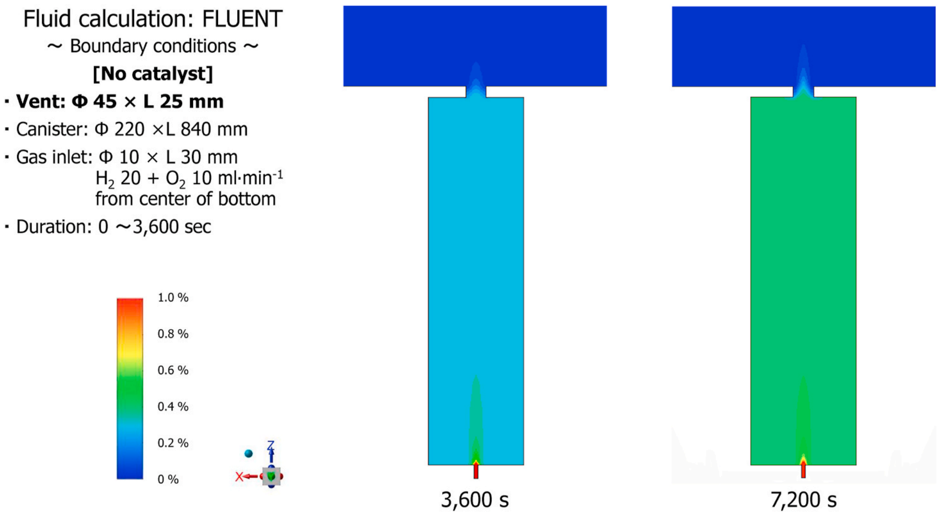


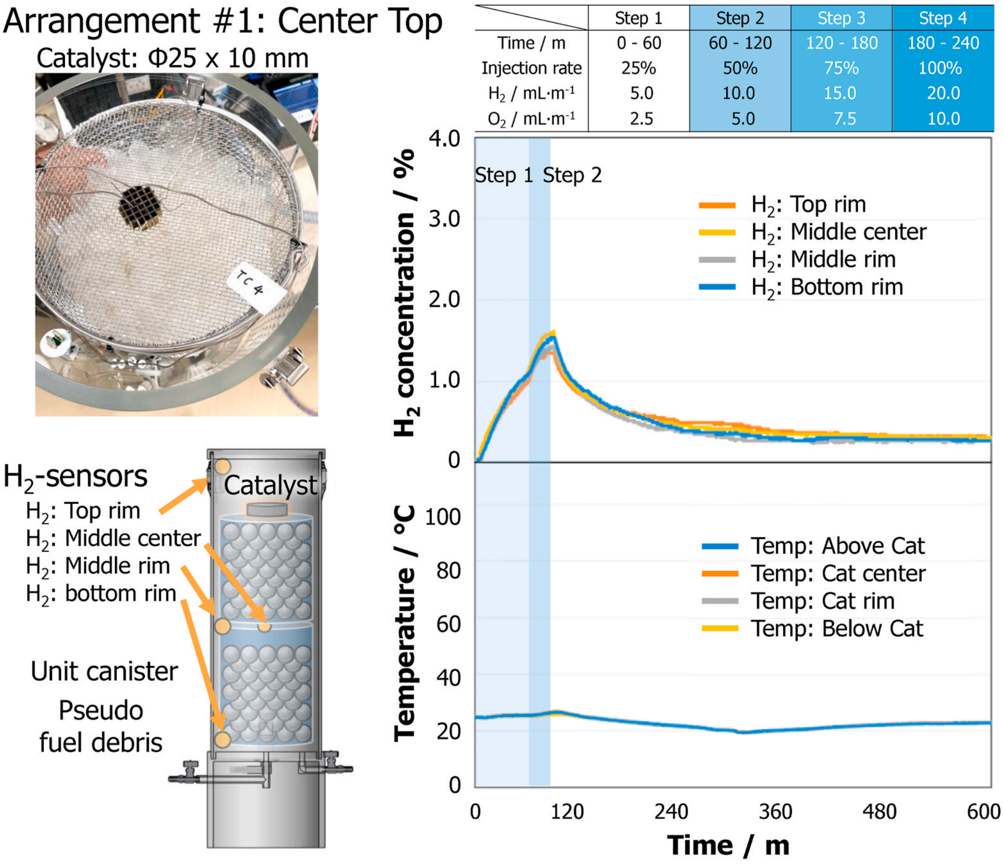
Fig. 6. Fluid analysis on H_2 concentration with wider and shorter ventilation.

(1) Arrangement #1: Catalyst Placement at Center Top

The catalyst was installed at the top of the fuel debris storage canister, directly above the center of the unit canister, and the temperature was measured at four points: the center of the catalyst bed, the rim of the bed, and about 5 mm above and below the center of the catalyst. The H_2 concentration was also measured at four points: the upper rim, middle rim, middle center, and bottom rim of the storage canister. According to the experimental procedure, 5.0 mL m^{-1} H_2 and 2.5 mL m^{-1} O_2 were injected for the first 60 min of the test. The amount of each injection was then doubled, and the H_2 concentration in the can increased, but there was no increase in the catalyst temperature, indicating that PAR does not work with this arrangement (Fig. 7).

(2) Arrangement #2: Two halves catalysts, at rim opposite

A catalyst with a diameter of 25 mm and a height of 10 mm was cut in the middle and arranged facing each other in the gap between the upper inner wall of the storage canister and the unit canister. H_2 and O_2 were injected according to the schedule in Table 1, and the temperature inside



	Step 1	Step 2	Step 3	Step 4
Time / m	0 - 60	60 - 120	120 - 180	180 - 240
Injection rate	25%	50%	75%	100%
H_2 / mL·m^{-1}	5.0	10.0	15.0	20.0
O_2 / mL·m^{-1}	2.5	5.0	7.5	10.0

Fig. 7. Catalyst configuration and arrangement #1: Center Top.

the catalyst bed rose immediately after the start of the test, but the increase in H_2 concentration was suppressed and stable, indicating that the catalyst was effective. The H_2 concentration gradually began to rise from Step 3, and when the test proceeded to Step 4, which corresponds to the published maximum predicted H_2 generation value 180 min after the start of the test, H_2 concentration began to rise, so the test was terminated. The temperature difference between the two catalysts was more than 45 °C, and it is considered that the reaction was uneven (Fig. 8-a).

(3) Arrangement #3: Two halves catalysts, at angle of 90°

This time, the catalyst divided into two was arranged at a right angle of 90°, and the temperature inside the catalyst bed rose, the increase in H_2 concentration was suppressed, and it was found that the catalyst was effective. The H_2 concentration was higher in Steps 1, 2, and 3 than in the opposing arrangement of #2, but the concentration remained constant in each step. However, H_2 concentration began to rise when moving to Step 4, so the test was terminated. It is estimated that the temperature difference between the two catalysts was more than 20 °C, causing uneven gas flow (Fig. 8-b).

(4) Arrangement #4: Two halves catalysts, at one sided

The two halves catalysts were arranged side by side on one side. Even at the maximum injection rate in Step 4, H_2 concentration was stable at about 1.5%, and the temperature of both catalysts rose uniformly, so it is considered that a good tumble flow was formed inside the storage

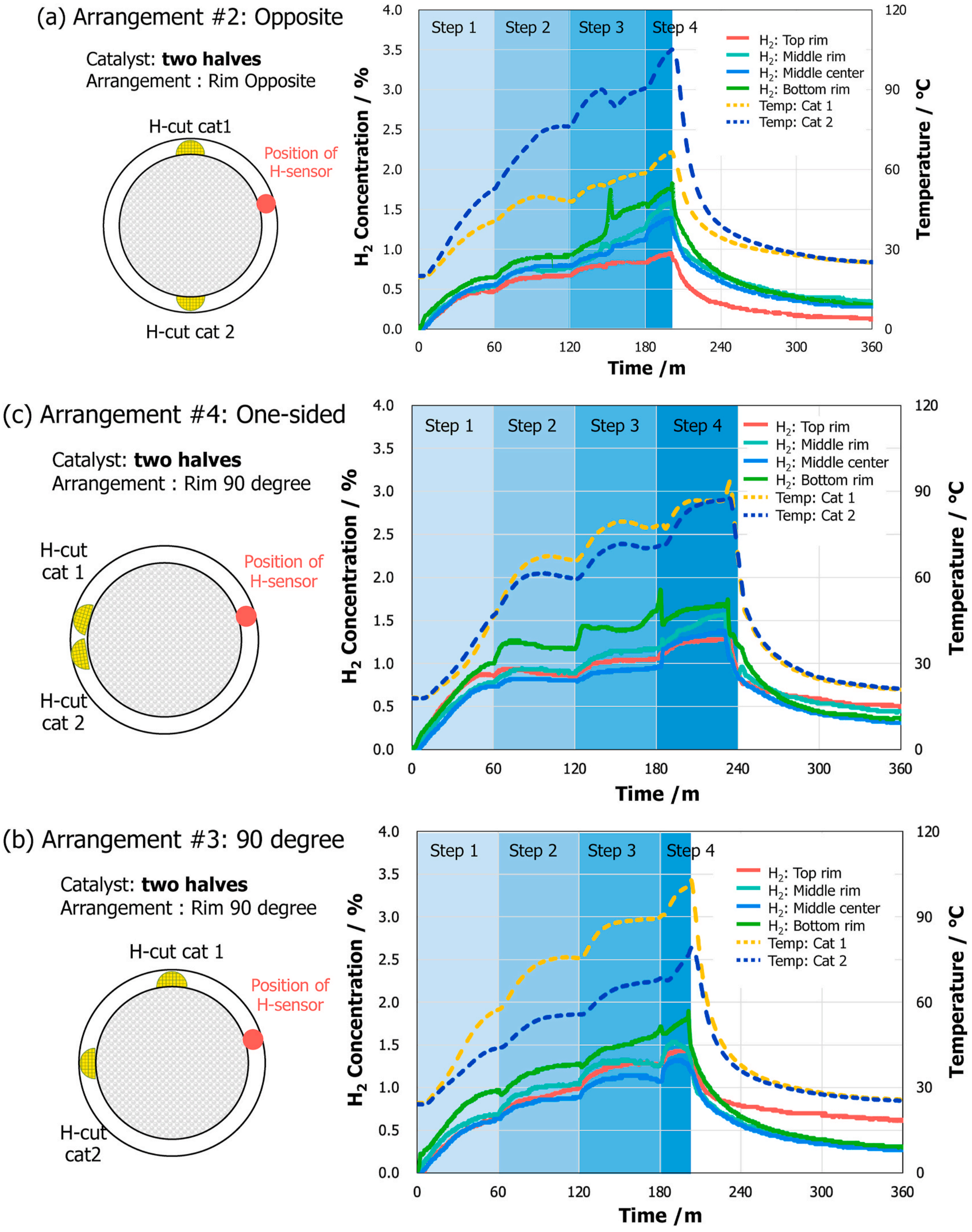


Fig. 8. Catalyst configurations and arrangements #2, #3, #4 and #5.

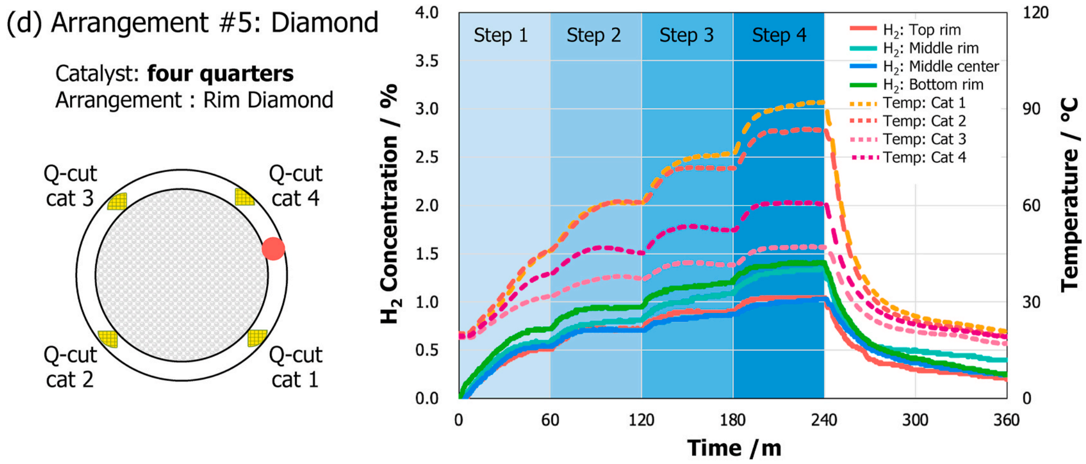


Fig. 8. (*continued*).

canister. The result provided important knowledge that it is effective to create strong natural convection by devising the catalyst arrangement (Fig. 8-c).

(5) Arrangement #5: Four quarters in diamond

Finally, the catalyst was divided into four and arranged in a diamond shape. The H_2 concentration was kept to the lowest in Steps 1, 2, 3, and 4, and even in Step 4, which corresponds to the maximum predicted H_2 generation, H_2 concentration was stable at 1.5%. However, the temperature difference between the four catalysts was large, and it can be said that there is room for improvement in the gas flow inside the can (Fig. 8-d).

The above five types of experiments showed that it is possible to optimize the catalyst arrangement and create a strong tumble flow by natural convection due to the H_2 oxidation reaction. It is effective to place the catalyst in the gap between the storage canister and the unit canister, rather than in the center. The cross-sectional area of the intelligent catalyst used in this study is small at 4.9 cm^2 and 4.9 cm^3, and the precious metal content is small at 5.9 mg. The catalyst itself is lightweight and easy to handle. This honeycomb-shaped intelligent catalyst has already been experimentally confirmed and reported to have good durability against high doses of radiation [29].

The passive autocatalytic recombiner, developed by applying automotive catalyst technology, has shown the possibility of reducing H2 concentrations while trapping both solid and gaseous substances containing radioactive materials during the seven-day transportation process, which is considered the most difficult of the technically challenging processes of fuel debris retrieval, transportation, and long-term storage in the Fukushima Daiichi decommissioning project.

4.3. *Natural convection and H_2 conversion velocities measurements using REKO-4*

It has already been reported that honeycomb-shaped PARs that use automotive catalyst technology have demonstrated good H_2 concentration reduction performance, and that this performance can be further improved by designing the shape, such as the density and thickness of the catalyst cells. This time, prototypes #7 and #3 were produced by further processing the config. #30 catalyst, as shown in Table 2.

Fig. 9 shows the natural convection velocity at a hydrogen concentration of 4% by volume, which has been determined using REKO-4. The solid markers indicate that a 300 mm high chimney is used, and the hollow markers indicate that no chimney is used. The water-repellent catalyst has a silicone coating on the bottom 2 mm of its 10 mm high, and is indicated by a red diamond marker and lettering. It can be seen that the presence or absence of water-repellent treatment does not affect the natural convection velocity. Even without a chimney, the natural convection velocity can be increased by decreasing the cell density and increasing the cell pore size, which is a very important experimental fact for applications in limited spaces such as fuel debris canisters.

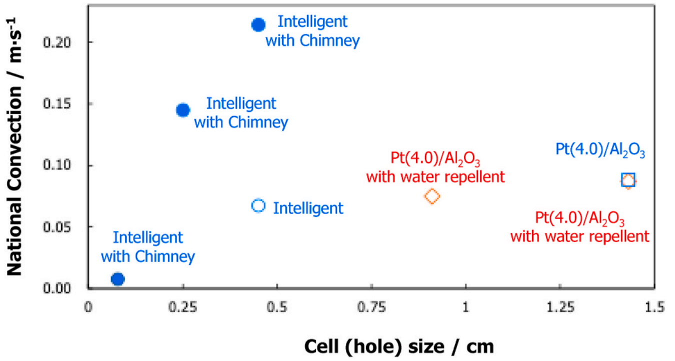


Fig. 9. Improvement of natural convection velocity by catalyst configuration.

Fig. 10 shows the hydrogen conversion rate per square centimeter of cross-sectional area for the Pt(4.0)/Al_2O_3 (config. #3) catalyst, which supports 4% platinum by mass on alumina. It can be seen that the hydrogen conversion is linearly affected by the concentration. The hydrogen conversion of the Pt(4.0)/Al_2O_3 catalyst of configuration #3 was 1.28 L h^{-1} cm^{-2} at an H_2 concentration of 4% by volume, and 0.59

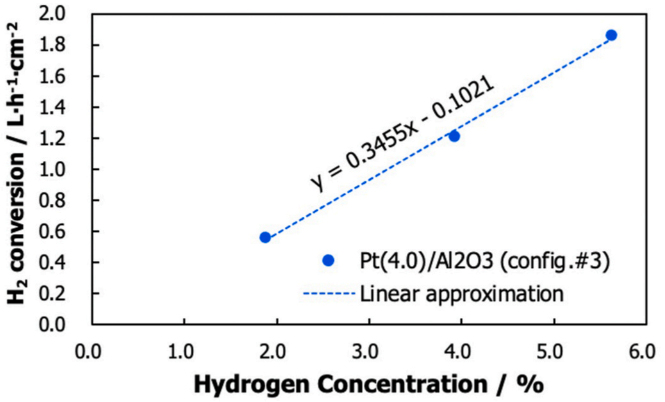


Fig. 10. Effect of concentration on hydrogen conversion per catalyst cross-sectional area.

L h^{-1} cm^{-2} at 2% by volume. The intelligent catalyst of #30, which was not machined, was 0.94 L h^{-1} cm^{-2} at an H_2 concentration of 4% by volume. The height of these catalysts is 1 cm, and no chimney is required. The maximum amount of hydrogen generated inside the fuel debris storage canister has been reported to be 1.1 L h^{-1}, so it is thought that a small catalyst with a cross-sectional area of about 1 cm^2 will be able to achieve the required hydrogen conversion efficiency. Taking into account a safety margin, it became clear that simply installing several catalysts with a diameter of about 1 inch (cross-sectional area of 5.0 cm^2) so that the gap between the inner wall of the fuel debris storage canister and the unit canister can be effectively used for gas convection can be expected to have a significant effect in reducing hydrogen concentration. Particular emphasis is placed on the importance of the catalyst configuration and its installation arrangement within the canister.

4.4. Reactivation test using REKO-4

From the results so far, it has become clear that a small catalyst can fully demonstrate its performance as a PAR for hydrogen safety. However, while examining various failure modes, it has become clear that in a closed, sealed environment, problems arise when hydrogen generation is discontinuous and intermittent, rather than when hydrogen is generated at a high concentration and high speed. Specifically, in an experiment with REKO-4, when the hydrogen supply to the pressure vessel in which the catalyst was installed was stopped and the vessel was left overnight, the hydrogen concentration fell below 1% and the reaction temporarily stopped. At this time, the inside of the pressure vessel became a high humidity, room temperature environment, and a problem emerged in which the catalyst would be difficult to reactivate if hydrogen was supplied again in a wet state. To address this issue, the results of a reactivation test in REKO-4 using Pt/Al_2O_3 (config. #3) catalyst, which is a further processed version of #30 catalyst, are shown in Fig. 11.

Here, the amount of Pt supported was set to 4% by mass relative to the alumina coat. Three of these Pt/Al_2O_3 (config. #3) catalysts with large holes, each 65 mm in diameter and 10 mm in height, were placed side by side (total volume of 99 cm^3), and after increasing H_2 concentration to 6% by volume at room temperature, all valves were closed and the reaction vessel was left for 20 h. At that time, H_2 concentration in the reaction vessel was 0.6% by volume, the temperature was 24.5 °C, and the relative humidity was 99.9%. After that, hydrogen was injected at room temperature and H_2 concentration was increased in 0.5% by volume increments. At 5.5%, the temperature of each of the three catalysts rose sharply and H_2 concentration dropped all at once. By devising the cell configuration of the catalyst, a clue was provided to solve the problem of catalyst reactivation at room temperature and high humidity, which had been an issue.

In addition, a similar reactivation test was also conducted on three Pt/Al_2O_3 (configuration 3) catalysts of the same shape, each with a water-repellent layer formed on the bottom (Fig. 12). Although there was variation between the three catalysts, reactivation occurred from H_2 concentration of 4%. However, since the reliability of the silicone coating in a high-dose radiation environment has not been ensured, this is only for reference.

5. Conclusion

In the decommissioning of the Fukushima Daiichi Nuclear Power Plant, the safe retrieval, transportation, and long-term storage of fuel debris are the biggest challenges Japan is facing. The greatest challenge is balancing the containment of radioactive materials with the reduction of the concentration of hydrogen generated, especially during the seven days required for open road transportation. This paper summarizes the challenges of hydrogen generation in sealed containers, research results, and a guide to the use of PAR in fuel debris storage canisters. The required characteristics of the PAR used here are completely different from those of the PAR used in the reactor building, and there is a serious problem that the water generated by hydrogen recombination has no escape route and the catalyst is always covered with a water film.

Based on publicly available drawings of fuel debris storage canisters, a full-scale transparent visualization canister was prototyped, and the catalytic effect during hydrogen generation was demonstrated by reproducing the actual usage environment. It was shown that the position of the catalyst is important to generate a circulating flow in sealed environment applications such as fuel debris storage canisters. The ventilation problem was clarified by both theoretical flow calculations and experiments.

A honeycomb catalyst was evaluated using large pressure vessel REKO-4 at FZJ, and the natural convection velocity due to the catalytic reaction was experimentally calculated. The catalyst configuration required to process the maximum amount of hydrogen generated in the storage canister was derived. It is expected that even a small catalyst with a cross-sectional area of about 1 cm^2 can maximize the conversion of hydrogen generated inside the fuel debris storage canister. A solution to the previously difficult issue of reactivation has also been demonstrated.

The fuel debris retrieval operation has just begun, with the first successful sampling taking place on November 7, 2024. The size of the removed fuel debris is reported to be approximately 9 × 7 mm, the weight was 0.693 g, and the dose rate (gamma rays) was approximately 8 mSv/h [35]. As the amount of fuel debris removed increases in the

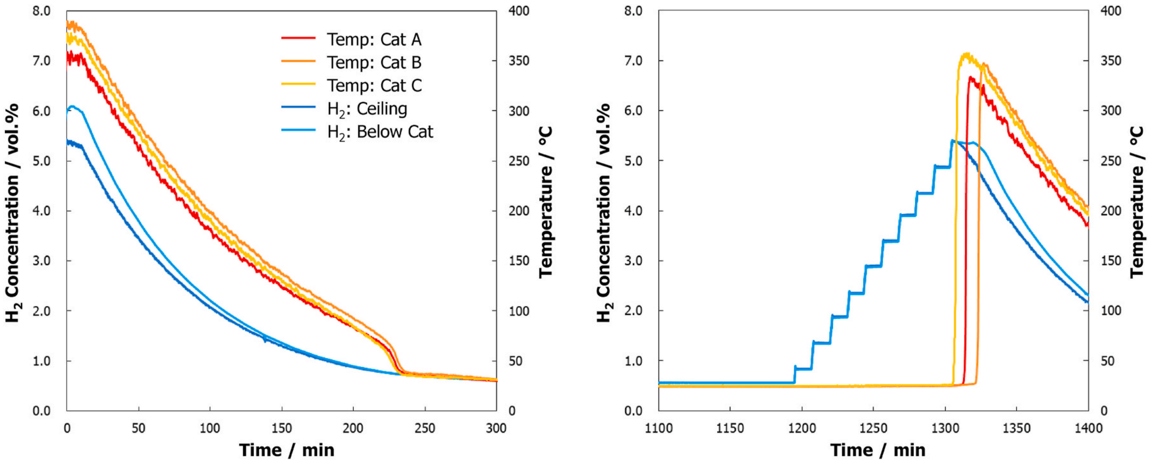


Fig. 11. Reactivation test for $Pt(4.0)/Al_2O_3$ (config. #3) at REKO-4.

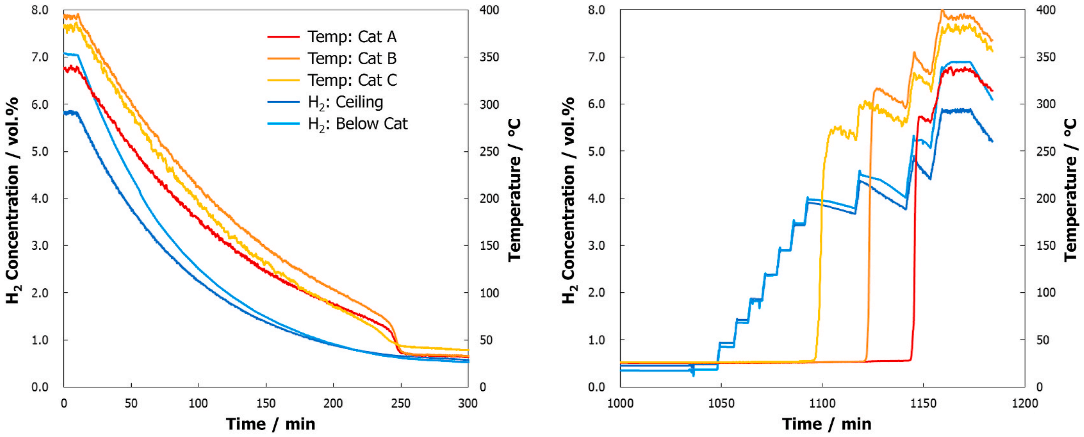


Fig. 12. Reactivation test for Pt(4.0)/Al_2O_3 (config. #3) with water-repellent layer at REKO-4.

future, technology to reduce the concentration of generated hydrogen will become increasingly important. The "passive autocatalytic recombiner," developed by applying automotive catalyst technology, is expected to contribute to reducing hydrogen concentrations in the decommissioning of the Fukushima Daiichi Nuclear Power Station. The results of this study emphasize that in order to effectively utilize this safety technology, it is important to understand the phenomenon and design the catalyst and installation method accordingly. Mutual cooperation among engineers involved in decommissioning work is highly desirable to ensure safety.

CRediT authorship contribution statement

Hirohisa Tanaka: Writing – original draft, Visualization, Supervision, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Sogo Iwata:** Data curation. **Tadasuke Yamamoto:** Data curation. **Tomohito Nakayama:** Data curation. **Shinya Uegaki:** Data curation. **Tomoaki Kita:** Data curation. **Atsuhiko Terada:** Visualization, Software, Methodology. **Daiju Matsumura:** Investigation, Formal analysis, Data curation. **Masashi Taniguchi:** Investigation, Data curation, Conceptualization. **Ernst-Arndt Reinecke:** Writing – review & editing, Supervision, Project administration, Investigation, Data curation, Conceptualization.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Abbreviations

1F	The Fukushima Daiichi Nuclear Power Station
ALPS	Advanced Liquid Processing System
IRID	International Research Institute for Nuclear Decommissioning ()
METI	Ministry of Economy, Trade and Industry ()
PAR	Passive autocatalytic recombiners
PCV	Primary Containment Vessel
REKO-T	Rekombinator-Transparent
RPV	Reactor Pressure Vessel
TCD	Thermal conductivity detector
TEPCO	Tokyo Electric Power Company Holdings, Inc.
TMI-2	Three Mile Island Nuclear Power Plant Unit 2

References

[1] Executive Summary of the Final Report, July 23, 2012. Investigation committee on the accident at Fukushima nuclear power stations of Tokyo electric power Company. https://www.cas.go.jp/jp/seisaku/icanps/eng/final-report.html; 2012.

[2] Lessons learned from the Fukushima nuclear accident for improving safety of U.S. Nuclear plants. National Academy Press; 2014. https://doi.org/10.17226/18294. ISBN 978-0-309-27253-7.

[3] Fukushima technical evaluation: phase 1- MAAP5 analysis, EPRI, palo alto, CA. 2013, 1025750.

[4] Fukushima Technical Evaluation. Phase 2 - potential for recriticality during degraded core reflood. Palo Alto, CA: EPRI; 2016, 3002005298.

[5] Tsuruda T. Nuclear power plant explosions at Fukushima-Daiichi. Procedia Eng 2013;62:71–7. https://doi.org/10.1016/j.proeng.2013.08.045.

[6] Katata G, Terada H, Nagai H, Chino M. Numerical reconstruction of high dose rate zones due to the Fukushima Daiichi Nuclear Power Plant accident. J Environ Radioact 2012;111:2–12. https://doi.org/10.1016/j.jenvrad.2011.09.011.

[7] NEA. Fukushima Daiichi nuclear power plant accident, ten years on: progress, lessons and challenges. Paris: OECD Publishing; 2021. https://www.oecd-nea.org/jcms/pl_56742/fukushima-daiichi-nuclear-power-plant-accident-ten-years-on?details=true.

[8] International Atomic Energy Agency. IAEA review of safety related aspects of handling ALPS-treated water at TEPCO's Fukushima Daiichi nuclear power station. Vienna: IAEA; 2022.

[9] International Atomic Energy Agency. IAEA international peer review mission on mid- and long-term roadmap towards the decommissioning of TEPCO's Fukushima Daiichi nuclear power station. Vienna: IAEA; 2019.

[10] https://www.mofa.go.jp/dns/inec/alps_navi07.html.

[11] https://www4.tepco.co.jp/en/decommission/progress/watertreatment/news/index-e.html.

[12] https://irid.or.jp/wp-content/uploads/2021/12/2020002Research_Report_Development_of_Technology_for_Containing_Transfer_and_Storage_of_Fuel_Debris.pdf.

[13] FY2020 Final Report (IRID public Japanese document) "Subsidies for decommissioning and contaminated water countermeasures (development of fuel debris collection, transport, and storage technology)" FY2018 supplementary budget.

[14] Tanaka H, Uenishi M, Tan I, Kimura M, Nishihata Y, Mizuki J. "An intelligent catalyst", SAE special publications-1573, advanced catalytic converters and substrates for gasoline emission systems (2001). Adv Three-way Cataly PT-123, SAE Trans: J Fuels Lubricants- 2001;110–4:986. https://doi.org/10.4271/2001-01-1301 *[SAE Technical Paper, 2001-01-1301 (2001*.

[15] Uenishi M, Taniguchi M, Tanaka H, Kimura M, Nishihata Y, Mizuki J, Kobayashi T. Redox behavior of palladium at start-up in the perovskite-type LaFePdOx automotive catalysts showing a self-regenerative function. Appl Catal B Environ 2005;57:267–73. https://doi.org/10.1016/j.apcatb.2004.11.011.

[16] Tanaka H, Taniguchi M, Uenishi M, Kajita N, Tan I, Nishihata Y, Mizuki J, Narita K, Kimura M, Kaneko K. Self-regenerating Rh- and Pt-based perovskite catalysts for

automotive-emissions control. Angew Chem Int Ed 2006;45:5998–6002. https://doi.org/10.1002/anie.200503938.

[17] Tanaka H, Taniguchi M, Kajita N, Uenishi M, Tan I, Sato N, Narita K, Kimura M. Design of the intelligent catalyst for Japan ULEV Standard. Top Catal 2004;30/31:389. https://doi.org/10.1023/B:TOCA.0000029780.70319.36.

[18] Tanaka H. An intelligent catalyst: the self-regenerative palladium-perovskite catalyst for automotive emissions control. Catal Surv Asia 2005;9:63. https://doi.org/10.1007/s10563-005-5992-2.

[19] Nishihata Y, Mizuki J, Akao T, Tanaka H, Uenishi M, Kimura M, Okamoto T, Hamada N. Self-regeneration of a Pd-perovskite catalyst for automotive emissions control. Nature 2002;418:164–7. https://doi.org/10.1038/nature00893.

[20] Nishihata Y, Mizuki J, Tanaka H, Uenishi M, Kimura. Self-regeneration of palladium-perovskite catalyst in modern automobiles. J Phys Chem Solid 2005;66:274–82. https://doi.org/10.1016/j.jpcs.2004.06.090.

[21] Matsumura D, Nishihata Y, Mizuki J, Taniguchi M, Uenishi M, Tanaka H. Dynamic structural change of Pd-perovskite automotive catalyst studied by time-resolved dispersive x-ray absorption fine structure. J Appl Phys 2010;107:124319. https://doi.org/10.1063/1.3437084.

[22] Matsumura D, Taniguchi M, Tanaka H, Nishihata Y. In situ X-ray absorption spectroscopy study on water formation reaction of palladium metal nanoparticle catalysts. Int J Hydrogen Energy 2017;42(11):7749. https://doi.org/10.1016/j.ijhydene.2016.08.189.

[23] Reinecke EA, Bentaib A, Kelm S, Jahn W, Meynet N, Caroli C. Open issues in the applicability of recombiner experiments and modeling to reactor simulations. Prog Nucl Energy 2010;52:136–47.

[24] Klauck M, Reinecke E-A, Kelm S, Meynet N, Bentaib A, Allelein HJ. Passive auto-catalytic recombiners ooperation in the presence of hydrogen and carbon monoxide: experimental study and model development. Nucl Eng Des 2014;266:137–47. https://doi.org/10.1016/j.nucengdes.2013.10.021.

[25] Morfin F, Sabroux JC, Renouprez A. Catalytic combustion of hydrogen for mitigating hydrogen risk in case of a severe accident in a nuclear power plant: study of catalysts poisoning in a representative atmosphere. Appl Catal 2004;B:47. https://doi.org/10.1016/j.apcatb.2003.07.001.

[26] Bachellerie E, Arnould F, Auglaire M, de Boeck B, Braillard O, Eckardt B, et al. Generic approach for designing and implementing a passive autocatalytic recombiner PAR-system in nuclear power plant containments. Nucl Eng Des 2003;221:151. https://doi.org/10.1016/S0029-5493(02)00330-8.

[27] Klauck M, Reinecke E-A, Allelein HJ. Effect of par deactivation by carbon monoxide in the late phase of a severe accident. Ann. Nucl Energy 2021;151:107887. https://doi.org/10.1016/j.anucene.2020.107887.

[28] 『TMI-2』GEND 062, Catalyst tests for hydrogen control in canisters of wet radioactive wastes. EG&G Idaho, Inc.; Aug., 1987.

[29] Eto J, Kawai M, Matsumoto M, Tanaka H, Hino R, Terada A, Taniguchi M, Sugiyama H. Experimental study of long-term catalytic effect on hydrogen generation G value of water by gamma-ray irradiation and hydrogen diffusion analysis in Compacted Hulls and End-Piece waste. J Radioanal Nucl Chem 2024. https://doi.org/10.1007/s10967-023-09251-2.

[30] Tanaka H, Masaki S, Aotani T, Inagawa K, Iwata S, Aida T, Yamamoto T, Kita T, Ono H, Takenaka K, Taniguchi M, Matsumura D, Reinecke E-A. An automotive intelligent catalyst that contributes to hydrogen safety for the decommissioning of Fukushima Daiichi nuclear power station (1FD). 2022. https://doi.org/10.4271/2022-01-0534. SAE Paper, 2022-01-0534.

[31] Ono H, Takenaka K, Kita T, Taniguchi M, Matsumura D, Nishihata Y, Hino R, Reinecke E-A, Takase K, Tanaka H. Research on hydrogen safety technology utilizing the automotive catalyst. E-J Adva Mainten 2019;11(No.1):40–5. ISSN-1883-9894/10.

[32] Reinecke E-A, Takenaka K, Ono H, Kita T, Taniguchi M, Nishihata Y, Hino R, Tanaka H. Performance tests of catalysts for the safe conversion of hydrogen inside the nuclear waste containers in Fukushima Daiichi. Int J Hydrogen Energy 2021;46:12511–21. https://doi.org/10.1016/j.ijhydene.2020.08.262.

[33] Tearada A, Nagaishi R. Effects of vent size and wind on dispersion of hydrogen leaked in a partially open space: studies by numerical analysis. Nucl Sci Eng 2023;197(4):647–59. https://doi.org/10.1080/00295639.2022.2126689.

[34] The technical strategic plan 2024 (Japanese version) published by the nuclear damage compensation and decommissioning facilitation corporation (NDF). 2024.

[35] Fuel Debris Portal Site, https://www.tepco.co.jp/en/decommission/progress/fuel-debris/index-e.html.