

Study of a Post-fire Verification Method for the Activation Status of Hydrogen Cylinder Pressure Relief Devices

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ABSTRACT

To safely remove from its fire accident site a hydrogen fuel cell vehicle equipped with a carbon fiber reinforced plastic composite cylinder for compressed hydrogen (CFRP cylinder) and to safely keep the burnt vehicle in a storage facility, it is necessary to verify whether the thermally-activated pressure relief device (TPRD) of the CFRP cylinder has already been activated, releasing the hydrogen gas from the cylinder. To develop a simple post-fire verification method on TPRD activation, the present study was conducted on the simple technique of verifying TPRD activation by measuring hydrogen concentration at the TPRD gas release port, using a catalytic combustion hydrogen densitometer and Type3 and Type4 CFRP cylinders having different linings. As a result, TPRD activation status can be determined by measuring hydrogen concentrations with a catalytic combustion hydrogen densitometer at the cylinder's TPRD gas release port.

INTRODUCTION

Carbon fiber reinforced plastic composite cylinders for compressed hydrogen (CFRP cylinders) are equipped with a thermally-activated pressure relief device (TPRD) capable of detecting heat and releasing gas to prevent the cylinder from bursting in a fire accident. Yet if the fire is extinguished before TPRD ever activates, the high-pressure gas is left inside the CFRP cylinder. To safely remove the vehicle from the accident site and to safety scrap the cylinder, it is necessary to verify whether the TPRD has already been activated and released the gas from the cylinder^{1), 2), 3)}.

While normally the internal pressure of a cylinder is verified by reading the pressure sensor connected to the cylinder, verification is often made impossible by the damaging of sensors and wirings in fire accidents. The conventional verification methods include visually observing any melting traces of the TPRD fuse metal (see Figure 1) and any burnout traces on the asphalt surface area below the TPRD gas release port (Figure 2)⁴⁾. Nevertheless the fuse metal vanishes in an intense fire; no burnout trace is left on the road surface when the gas is released upward. Consequently it is necessary to develop a new method of verifying TPRD activation.

To develop a simple, quick verification method, the present study was conducted on the possibility of judging TPRD activation status by measuring any residual gas at the TPRD release port using a hydrogen densitometer.



Fig.1 Traces of molten fuse metal



Fig.2 Burnout traces on asphalt road

TEST METHOD

A flame exposure test simulating a vehicle fire accident was carried out on stand-alone CFRP cylinders. The test cylinders, Type3 and Type4, were each exposed to flames, whereby the TPRD was activated and the residual gas was measured at the release port with a hydrogen densitometer in time sequence. Figure 3 shows the overview of the test setup, and Figure 4 the appearance of TPRD attached to the cylinder. Table 1 shows the test conditions applied.

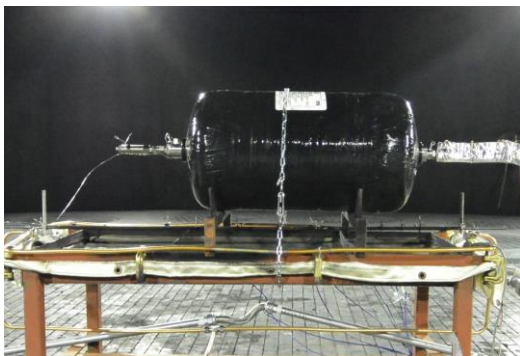


Fig.3 Overview of test setup

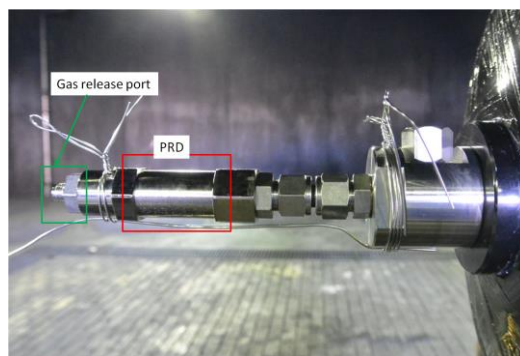


Fig.4 Appearance of TPRD

Table 1 Test conditions

Cylinder	Type3 (28litter, ϕ 280mm, Length 730mm) Type4 (65litter, ϕ 400mm, Length 830mm)
PRD type	Thermally-activated pressure relief device (TPRD)
Hydrogen gas sensor Type	Detector : Thermal Conductivity Gas Sensors, Diffusion type) Detector : Catalytic Combustion Sensors, (Vacuum type)
Cylinder pressure	1.5MPa
Gas release diameter	1/4 inch
Fire test conditions	Localized Fire Exposure:10min, Engulfing Fire:50min (Temp. control : HFCV-GTR No.13)
Sensor location	Gas release port

To enable the verification of TPRD activation even in accident situations where gas diffusion from the cylinder is easier, stricter flame exposure test conditions were applied with regard to piping structure, hydrogen pressure and vehicle damage. As for the piping structure, TPRD and its gas release port were connected in a straight line while the inner diameter of the gas release port was set at 4.57 mm. The hydrogen was pressurized at 1.5 MPa, the minimum necessary pressure for TPRD activation⁵⁾. Regarding the flame exposure conditions, a cylinder temperature environment was adopted in accordance with the test method of the Global Technical Regulation for Hydrogen Fuel Cell Vehicles (HFCV-GTR) which was based on the vehicle flame exposure test data obtained by the Japan Automobile Research Institute and US automobile manufacturing companies^{6), 7)}.

The CFRP cylinder was exposed to localized flames for 10 min, then to engulfing flames for as long as 50 min. The flames were produced by a propane gas burner as prescribed in HFCV-GTR in order to heat the whole area of the cylinder to uniform temperatures⁸⁾ (burner size : 1650mm×900mm). In view of the findings that in a vehicle total-loss fire accident the full-scale fire in the engine room, passenger room or trunk room lasts for no more than 1 hour^{9), 10)}, the maximum fire exposure time of the CFRP cylinder was set at 1 hour (10 min localized fire + 50 min engulfing fire). Two types of hydrogen densitometers were employed: first the thermal conductivity gas sensors type (measurement range of 0~100vol%; accuracy of full scale $\pm 5\%$), and second the catalytic combustion sensors type (measurement range of 0~10,000 ppm; accuracy of full scale $\pm 5\%$). The thermal conductivity gas sensors type was used when the detected hydrogen concentration exceeded 2vol%, while the catalytic combustion sensors type was used for 2vol% or less. Before the test start, it was confirmed that no hydrogen gas was detectable at the TPRD gas release port.

RESULTS AND DISCUSSION

Results of Type3 cylinders

Figure 5 shows the view of the fire exposure test on the Type3 cylinder.

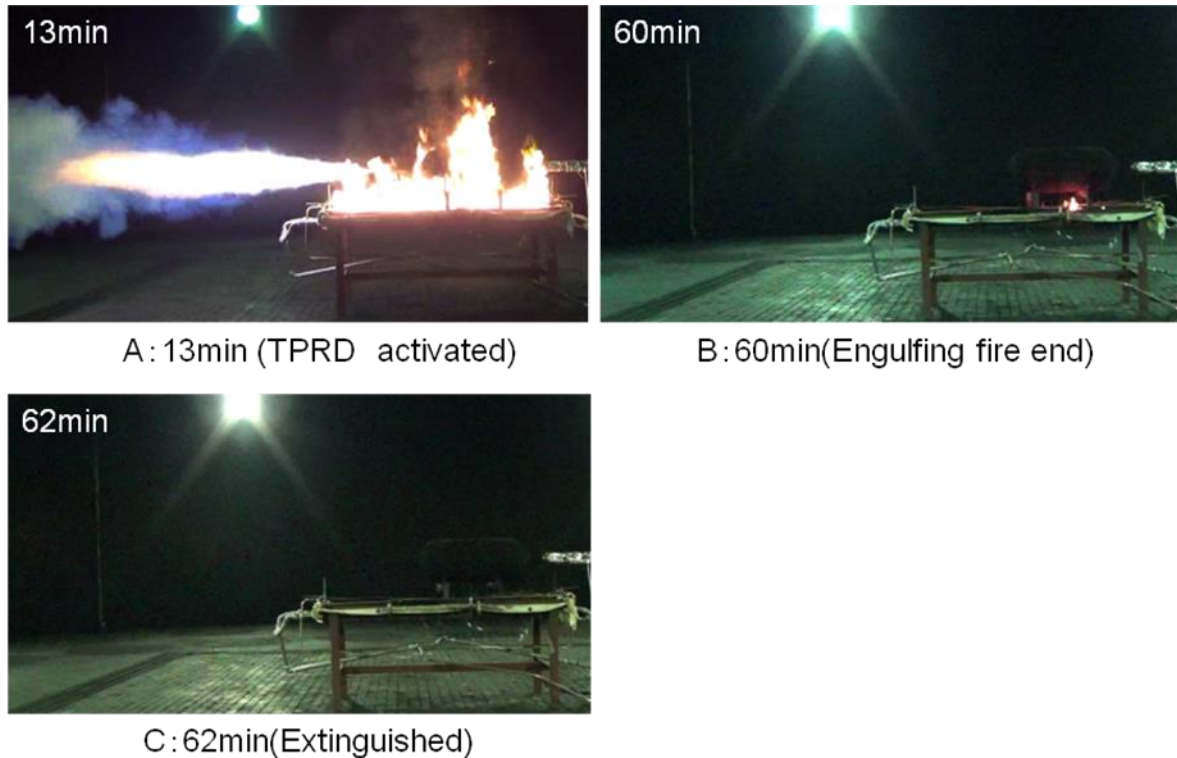


Fig.5 Fire exposure test scenes (Type3)

The TPRD of the Type3 cylinder activated about 13 min after the test start (10 min localized fire + 3 min engulfing fire), with the hydrogen releases forming intense flames as shown in the Figure 5. The propane gas burner was turned off at the completion of the test (10 min localized fire + 50 min engulfing fire), whereby the flames on the Type3 cylinder quickly became extinct. The post-fire measurements by a hydrogen densitometer at the TPRD gas release port were as shown in Table 2 and Figure 6. The body temperatures of the CFRP cylinder and the TPRD lowered to the outdoor temperature levels in about 5 hours.

Table 2 Hydrogen gas concentration (Type3)

Time	Hydrogen gas Conc.	Sensor type
2h	32Vol.%	Thermal Conductivity Gas Sensors
1day	25Vol.%	Thermal Conductivity Gas Sensors
1week	11Vol.%	Thermal Conductivity Gas Sensors
1month	3500ppm	Catalytic Combustion Sensors

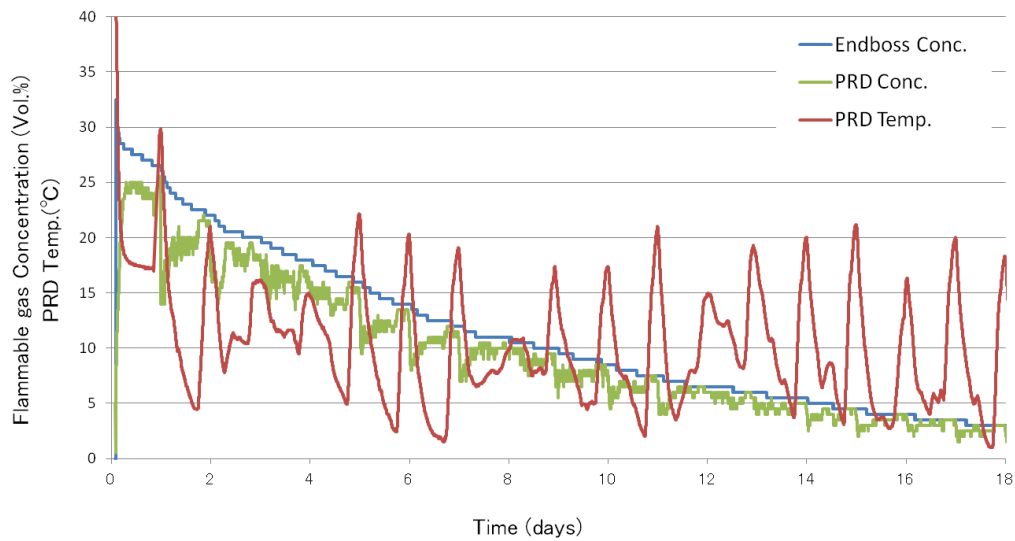


Fig.6 Hydrogen gas concentration in time (Type3)

For the Type3 cylinder, the measurements by the thermal conductivity gas sensors hydrogen densitometer proved to be 25vol% one day after fire extinction, 11vol% one week after, and non-quantifiable one month after. Yet the other catalytic combustion hydrogen densitometer detected 35,000 ppm a month after, indicating that, depending of hydrogen densitometer types, hydrogen gas at the TPRD release port remained detectable one month after fire extinction. As shown in Figure 6, both hydrogen concentration at the TPRD gas release port and the body temperature of TPRD varied in the first 18-day period. Hence it was interpreted that the in-cylinder gas underwent a repeated expansion and contraction process in keeping with the variations in outdoor temperature; whereby the gas was gradually replaced and diluted by the air outside.

Results of Type4 cylinders

Figure 7 shows the view of the fire exposure test on the Type4 cylinder.

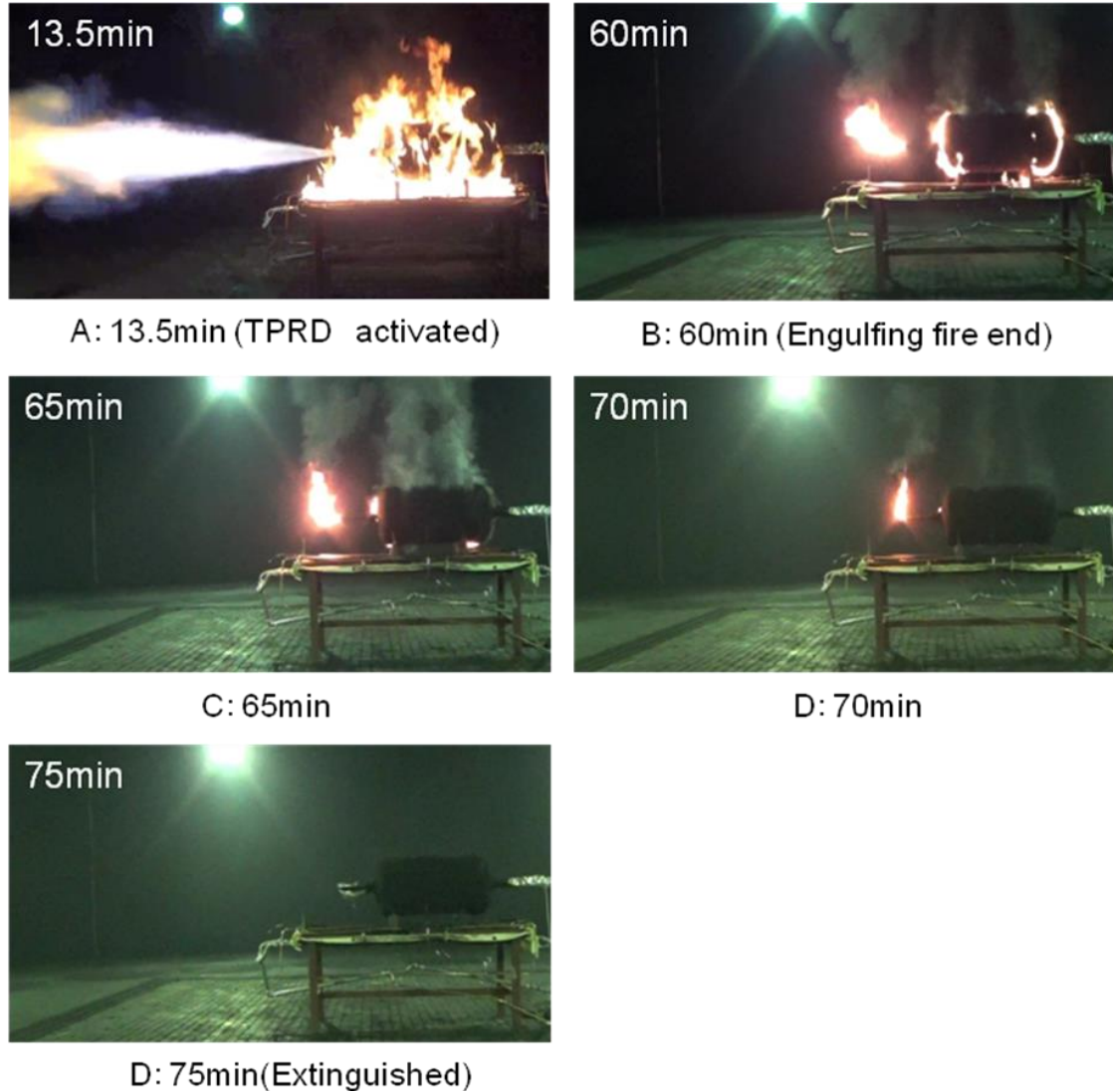


Fig.7 Fire exposure test scenes (Type4)

The TPRD of the Type4 cylinder activated about 13.5 min after the test start (10 min localized fire + 3.5 min engulfing fire), with the hydrogen releases forming intense flames as shown in the Figure 7. The propane gas burner was turned off at the completion of the test, after which the Type4 cylinder burned for about 15 min more (Figure 7, D). Unlike the Type3 cylinder which showed the blue flames of hydrogen releases, the flames of releases from the Type4 cylinder was bright yellow, the phenomenon attributable to the gasification of the resin lining and mixing of this gas with hydrogen inside the cylinder. Consequently it was assumed that the gas detected at the TPRD release port after fire extinction was mostly the unburnt gas generated from the resin lining, rather than residual hydrogen gas. Table 3 shows the hydrogen gas

concentrations of the Type4 cylinder as measured after fire extinction.

Table 3 Hydrogen gas concentration (Type4)

Time	Hydrogen gas Conc.	Sensor type
2h	> 10000ppm	Catalytic Combustion Sensors
5h	> 10000ppm	Catalytic Combustion Sensors
24h	3000ppm	Catalytic Combustion Sensors
72h	non-quantifiable	Catalytic Combustion Sensors

In case of the Type4 cylinder, post-fire gas levels could not be detected by the thermal conductivity gas sensors hydrogen densitometer, but the catalytic combustion hydrogen densitometer detected 10,000 ppm or more hydrogen even 5 hours after fire extinction and 3,000 ppm at 24 hours after. The gas proved non-quantifiable at 72 hours after fire extinction. The difference of Type3 and Type4 result is due to the liner materials. Since the working principle of catalytic combustion hydrogen densitometers is to measure the temperature rise of a platinum coil when gas undergoes contact combustion on a catalytic surface¹¹⁾, the flammable gas generated from the heated resin lining and mixed with the hydrogen gas can be detected. It is therefore considered possible to verify TPRD activation, using a catalytic combustion hydrogen densitometer.

CONCLUSIONS

To develop a simple method of verifying TPRD activation at post-fire accident sites, the present study was conducted on a verification technique based on the measurement of hydrogen concentration at the TPRD gas release port, using a hydrogen densitometer. It was found that when a catalytic combustion hydrogen densitometer was used, hydrogen concentrations exceeding 3,000 ppm could be measured continuously for about a month in the case of Type3 and for about 24 hours in the case of Type4 cylinders even under the hostile test conditions of a vehicle burn-down fire accident and the TPRD piping structured to allow greater gas diffusion from the cylinder. Consequently it was concluded that TPRD activation status can promptly be determined by measuring hydrogen concentrations with a catalytic combustion hydrogen densitometer at the cylinder's TPRD gas release port.

In addition, we have verified this method in the FCV. As a result, it was confirmed that this method was valid.

Finally, the present study was carried out as part of the "technology development project for hydrogen production, transport and storage systems" commissioned by New Energy and Industrial Technology Development Organization (NEDO), a national research and development agency of Japan.

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