The Passive Autocatalytic Recombiner Test Program at Sandia National Laboratories

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Abstract
Sandia National Laboratories (SNL) has developed systems and methodologies to measure the amount of hydrogen that can be depleted in a containment by a passive autocatalytic recombiner (PAR). Experiments were performed that determined the hydrogen depletion rate of a PAR in the presence of steam and also evaluated the effect of scale (number of cartridges) on the PAR performance at both low and high hydrogen concentrations.

Introduction
PARs are being considered by the nuclear power industry as a combustible gas control system in operating plants and advanced light water reactor (ALWR) containments for design basis events. PARs do not require a source of power; instead, they use a catalyst to recombine hydrogen and oxygen gases into water vapor upon contact with the catalyst. At low hydrogen concentrations, energy from the recombination of hydrogen with oxygen is released at a relatively slow (but continuous) rate into the containment. The heat produced creates strong buoyancy effects which increases the influx of the surrounding gases to the recombiner. These natural convective flow currents promote mixing of combustible gases in the containment.

SNL, under the sponsorship and direction of the U.S. Nuclear Regulatory Commission (USNRC), has conducted an experimental program to evaluate the performance of PARs. A PAR was tested at the Surtsey experimental test facility at SNL. The following describes the configuration of the PAR, the test facility, the instrumentation, the control and data acquisition system, the test conditions, and the test results and analyses.

PAR and Test Facility Description
The PAR test module was a scaled version of the prototype PAR that was developed and fabricated by NIS INGENIEURGESELLSCHAFT MBH (Hanau, Germany). Detailed tests and analyses were made in cooperation with the Battelle Institute, Frankfurt, and the Technical University, Munich [1]. Its development has been sponsored by the German utility, RWE Energie. The NIS/RWE PAR device contains flat rectangular cartridges filled with porous
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spherical ceramic pellets, which are coated with palladium. The large surface area of the palladium layer of the pellets acts on diffused gas molecules to recombine hydrogen with oxygen. Between the cartridges, the PAR device has open flow channels to allow heavier particles or aerosols in the atmosphere to flow through with little plugging of the cartridge and little fouling of the pellet surface.

The prototype PAR contained two rows of standard catalytic cartridges (44 cartridges per row) and had dimensions of 1 m by 1 m. The PAR test module (also manufactured by NIS) contained only one row of standard catalytic cartridges and could be assembled as either a 1/2 scale (44 cartridges), 1/4 scale (22 cartridges), or 1/8 scale (11 cartridges) PAR by removing cartridges and using smaller (length) front and back panels. Note that the 1/2 scale PAR test module configuration has dimensions of ~0.5 m by ~1.0 m.

Figures 1 and 2 show that the PAR test module housing holds the catalyst cartridges in a vertical direction and guides the air flow. A vertical flow channel of about 1-cm spacing is formed between the cartridges. These flow channels (along with the PAR body or housing) define the flow area for convection of the heat generated by the heat of reaction. The PAR exit has a chimney with a free cross-sectional area equal to the cross-sectional area through the cartridges.

The catalyst material is inserted into rectangular cartridges (0.45 m length, 0.01 m wide, 0.20 m tall). The cartridges are filled with the catalyst pellets. The steel sides of the cartridges are perforated with many slot-like openings that allow gases to enter the cartridge and steam to exit. The catalyst is a palladium-coated (0.5 w/o) aluminum oxide pellet with a diameter of about 4-6 mm and a bulk density of ~0.5 g/cc. The porous oxide pellet provides a large inside surface area (~100 m²/g) of palladium that allows a high conversion. A hydrophobic coating is placed on each pellet to minimize startup delays due to water, either from steam condensation or from containment sprays, on the catalyst surface.

Figure 3 shows the location of the PAR test module in the Surtsey vessel. The PAR was located at the vessel centerline, ~1 m above the midline elevation in the Surtsey vessel. Horizontal and vertical I-beams exist in the lower half of the Surtsey vessel but there are no I-beams located directly below the PAR. The Surtsey vessel is an insulated ASME-approved steel pressure vessel with a current working internal volume of 99 m³. It has a cylindrical shape with removable, dished heads attached to both ends, and is 3.6 m in diameter by 10.3 m high.

**Instrumentation, Control, and Data Acquisition**

The most significant variables measured in the PAR experiments were: (1) the pressure and temperature in the Surtsey vessel, (2) the gas constituents and steam concentrations, (3) the PAR pellet and channel gap temperatures, (4) the flow velocity through the PAR, and (5) the amounts of hydrogen and oxygen injected into the Surtsey vessel. A personal computer (PC)-based data acquisition system (DAS) was designed to control and monitor the course of the test in real-time. The DAS provided instantaneous readouts of the temperatures of the cartridge pellets and corresponding cartridge air gaps, Surtsey vessel pressure, temperatures, and gas concentrations, and valve positions for steam, hydrogen, and oxygen additions. In addition, the DAS controlled
the hydrogen target concentration and gas addition interval. This allowed changing the test conditions (during the course of a test) based on real-time test results.

Four pressure transducers were used to measure the pressure in the Surtsey vessel. The gas temperature in the Surtsey vessel was measured with twenty thermocouples installed in two rakes. The two thermocouple rakes (10 thermocouples each, 1-m spacing) were installed vertically in the vessel; one rake at the vessel centerline (array A) and one rake (array B) located about 0.32 m from the vessel wall. In addition, thermocouples measured the Surtsey wall temperature and the injected oxygen, hydrogen, and steam temperatures. Steam was mixed with the oxygen and/or hydrogen during each gas injection to minimize steam condensation.

A real-time gas mass spectroscopy (GMS) system was used to determine the concentrations of nitrogen, oxygen, and hydrogen in the vessel at four sample points. The four sample points were at the PAR inlet, the PAR outlet, high in the vessel near the dome, and low in the vessel near the floor. Gas grab samples were used as an independent verification of the gas composition.

A color camera and an infrared (IR) camera were mounted on Surtsey ports and viewed the PAR through tempered glass windows. In addition to the digital camera, an infrared camera also viewed the PAR through a different level 5 port. The cameras could see the PAR exit (top of the chimney) and provide visual evidence in the event of a deflagration event. Other instrumentation included a hygrometer to measure relative humidity and pitot-tube differential pressure transducers and a hot-wire anemometer to measure the velocity of the gas at the PAR inlet and outlet.

Twelve thermocouples monitored the catalyst temperature at three cartridge locations; PAR middle (and a PAR middle backup), PAR edge, and PAR corner. Three vertical positions for temperature measurement were monitored at each location (2-cm from the bottom, middle, and 2-cm from the top). These thermocouples were inserted into the cartridges and surrounded by the catalyst pellets. Twelve thermocouples monitored the temperature of the gas in the gap between the cartridges and were located opposite of the catalyst thermocouples. Four thermocouples monitored the PAR inlet temperature. Two thermocouples were located at the centerline middle and two were located at the centerline edge (within 2-cm of the PAR bottom). Four thermocouples monitored the PAR outlet temperature. Two thermocouples were located at the centerline middle and two were located at the centerline edge (within 2-cm of the chimney exit).

The hydrogen and oxygen gas was supplied to the vessel from separate manifolds. Standard 44 liter compressed gas cylinders were installed on the manifolds. In the tests that involve a prototypic air/steam atmosphere, the cold gas entering the vessel was mixed with an appropriate amount of steam (capable of heating the cold gas to saturation temperature) using a diffuser/mixer pipe that was located near the floor of the vessel. This was necessary to prevent condensation of the steam. Mass flow controllers were used to provide precise metering of the hydrogen and oxygen into the vessel. Two mixing fans were installed in the vessel. They were located on opposite sides of the PAR at the openings of the I-beam lattice; one pointed upward
and one pointed downward. The fans were usually operated when hydrogen was injected and prior to taking gas grab samples to ensure that the containment atmosphere was well mixed.

**Gas Composition Measurements and Analyses**

The GMS system cannot measure gas concentrations in the presence of steam; a dry sample must be presented. In order to achieve this, a condenser and condensate trap (and heated gas inlet lines) were installed on each gas measurement line. This yielded dry-basis gas concentrations; however, to determine wet-basis gas concentrations, the steam fraction must be known. A hygrometer was used to determine the relative humidity (RH). The steam concentration was then calculated from the ratio of saturation pressure to total pressure times the RH fraction. The saturation pressure of steam was determined from saturated steam tables using the vessel average gas temperature.

**Test Matrix**

Six depletion rate tests using a scaled PAR were conducted. PAR performance at low hydrogen concentrations was determined at 1/2 scale, at 1/4 scale, and at 1/8 scale. NIS states that the hydrophobic coating is probably destroyed when the PAR catalyst exceeds temperatures of about 473 K. The PAR catalyst would reach these temperatures at about 2% H₂ in cold dry air and about 1% H₂ in a 50 mole % air/50 mole % steam environment at 0.2 MPa. These tests were performed at hydrogen concentrations that would not destroy the hydrophobic coating.

Three repeat tests (at 1/2 scale, at 1/4 scale, and at 1/8 scale) were performed at relatively high hydrogen concentrations which yielded the scaled performance data and completed the scaled depletion rate test series.

**Experimental Results**

The scaled depletion rate tests started with a mixture of 0.107 MPa of air and 0.107 MPa of steam, for a total pressure of about 0.21 MPa. To achieve these conditions, the vessel was sealed with about 0.083 MPa of cold air inside (one Albuquerque atmosphere at about 293 K). The Surtsey vessel was then heated internally by adding steam to obtain a gas temperature of about 375 K. At a temperature of 375 K, the air and steam partial pressures become equal.

Two observations can be made regarding most of the PAR tests. An evident depletion rate (startup) was achieved by the PAR within 10 minutes in hot, steamy atmospheres when exposed to hydrogen concentrations in the range of 1 to 6 mole %. The second observation was that at steady-state operation the PAR appeared to generate a convective flow loop in the Surtsey vessel from the PAR outlet to the dome, down the Surtsey wall (until reaching the height of the PAR inlet), and then returning to the PAR inlet; as indicated by both the hydrogen concentration and the vessel gas temperature measurements. Since the convection flow pattern did not extend to the lower half of Surtsey vessel, the vessel was not completely well-mixed by the PAR during steady-state operation. The hydrogen concentration from the sample point located near the floor always showed a higher concentration when measurements were taken after the last addition, as compared to the other sample points. This indicated that the depletion below the PAR near the floor was lower than that in the upper half of the Surtsey vessel. Also, the convective loop
appeared to be driven further downward into the lower half of the Surtsey vessel in those tests with the higher hydrogen concentrations and hence higher PAR temperatures.

A test with the PAR configured at 1/8 scale provides an example of a PAR performance test. The Surtsey vessel was sealed and pressurized with steam to about 0.21 MPa. The initial gas temperature was about 374 K. The PAR started recombining after the first hydrogen addition to about 1.0 mole % which is indicated by the first small increase of the catalyst temperature (Figure 6). There was about a ten minute delay (from the time of first hydrogen injection) in PAR startup. The startup of the PAR is characterized by the establishment of natural convection, which is shown by the increase in the gas temperature at the PAR outlet (Figure 7), followed by the increase in the vessel gas temperature (Figures 4 and 5). Figure 5 also shows the times when the mixing fans were operating while Figure 7 shows the hydrogen additions using the mass flow controller. Figure 8 gives the wet-basis gas concentrations. The steam concentration ranged from about 50 mole % at the beginning of the test to about 40 mole % at the end. The oxygen concentration remained relatively constant at about 10 mole %. Figure 9 focuses on the hydrogen concentrations at the vessel floor, PAR inlet, PAR outlet, and vessel dome locations. This figure also shows the integrated hydrogen addition. The hydrogen concentration from the sample point located near the floor showed smaller decreases as time progressed after the last addition, compared to the other sample points. This indicated that a reduced depletion occurred in the lower half of the Surtsey vessel, below the PAR elevation.

**PAR Performance Analyses**

Hydrogen depletion rates are used to measure the performance of a PAR. The hydrogen depletion rate is usually determined as a function of the hydrogen concentration in the vessel. Depletion rate analyses can also be used to show the effect of various factors, such as PAR location, oxygen concentration, catalyst poison, etc., on PAR performance.

The following procedure was used to determine the depletion rate. First, the time-dependent amount of hydrogen in the Surtsey vessel (in moles) was determined by multiplying the average hydrogen concentration by the total number of moles in the Surtsey vessel. The average hydrogen concentration was assumed to be that measured by the gas mass spectrometer at the PAR inlet sample point. The total number of moles in the vessel was calculated using the average gas temperature (determined from the array B thermocouples) and the ideal gas law.

The methodology used to determine the depletion rate assumed that the vessel was well-mixed; this introduced some error since the average hydrogen concentration was not actually measured and cannot be calculated since the local steam concentrations were not known. The measured depletion rates may slightly overpredict hydrogen depletion at the stated hydrogen level since the hydrogen concentration at the PAR inlet sample point, just before the fans were turned on, was lower than the average value. The depletion rate was then determined by calculating the difference in hydrogen moles at each successive time interval, using the data from the steady-state depletion interval, after the hydrogen additions were stopped. The calculated depletion rate was then plotted against the measured hydrogen concentration.
PAR performance and the effects of scale were determined with tests at both low and high hydrogen concentrations. Note that the initial conditions for all tests started with a vessel pressure of about 0.2 MPa, with approximately 50/50 mixtures of air and steam. Preliminary test results indicate that the 1/2 scale depletion rate was ~4 times the 1/8 scale depletion rate.

A comparison of the scaled depletion rate data can be made by normalizing the data. Depletion rate models predict that depletion rate is directly proportional to scale and depletion rate is independent of volume. Therefore, a simple scale factor can be used to normalize the data. Figures 10 shows the scaled depletion rate data normalized to full-scale by applying the scale factor (x2 for 1/2 scale, x4 for 1/4 scale, and x8 for 1/8 scale).

Summary
Hydrogen depletion rates using a scaled PAR were measured in the Surtsey test vessel at Sandia National Laboratories. The experiments were used to determine the hydrogen depletion rate of a PAR in the presence of steam and also to evaluate the effect of scale (number of cartridges) on the PAR performance at both low and high hydrogen concentrations.

The following additional conclusions can be made. The PAR started within 10 minutes in hot, steamy atmospheres when exposed to hydrogen concentrations in the range of 1 to 6 mole %. The PAR appeared to generate a convective flow loop in the Surtsey vessel from the PAR outlet to the dome, down the Surtsey wall until reaching a height near the PAR inlet, and then returned to the PAR inlet.

References

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Figure 1. Bottom view of the PAR housing and chimney with one cartridge.

Figure 2. Cartridges held in a vertical configuration by the PAR housing.

Figure 3. PAR location in the Surtsey vessel.

Figure 4. Centerline gas temperatures with 1/8 scale PAR.
Figure 5. Wall gas temperatures with 1/8 scale PAR.

Figure 6. Catalyst cartridge temperatures with 1/8 scale PAR.

Figure 7. Inlet and outlet temperatures with 1/8 scale PAR.

Figure 8. Gas concentrations (wet-basis) with 1/8 scale PAR.

Figure 9. H₂ concentrations (wet-basis) with 1/8 scale PAR.

Figure 10. Normalized hydrogen depletion rates as a function of hydrogen concentration.