CHEMICAL ENGINEERING TRANSACTIONS
VOL. 90, 2022

A publication of
AIDIC
The Italian Association of
Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Aleš Bernatík, Bruno Fabiano
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ISBN 978-88-95608-88-4; **ISSN** 2283-9216

DOI: 10.3303/CET2290022

Passive Autocatalytic Recombiners as Explosion Prevention and Mitigation Tool in Hydrogen Energy and Transport Infrastructures

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Passive Autocatalytic Recombiner (PAR) is of vital importance for hydrogen explosion prevention and mitigation at the nuclear power plants under severe accident conditions. From the early stage of PAR technology research and development in 1980-th the different types of recombiners have been proposed and tested at different scales. One of the mentioned recombiner type - namely self-intake PARs – now are widely used for hydrogen safety provision at the PWR, VVVR and CANDU nuclear power plants. Report goals are – 1) to briefly describe the history, motives for development of the different basic PAR types and their pros/cons for nuclear applications, 2) to argue - why the further PAR development can be valuable means outside of the nuclear applications, specifically, in the hydrogen energy and transport infrastructure safety? Joint (by engineering communities in the process industries and in the nuclear energy) development of the third generation of the inherently safe PARs and their appropriate technical standardization (in terms of performance and safety margins) by the international bodies can be valuable and effective step for global hydrogen energy and transport promotion and acceptance.

1. Introduction

Hydrogen as an energy carrier can bring benefits - in terms of global warming prevention, carbon emissions reduction and energy efficiency increase – during transition from the hydrocarbon-based to carbon-neutral energy and transport. To promote hydrogen as a reliable, next-generation fuel to power cars/ships/airplanes, heat homes and generate electricity it is necessary to cope with the multiple political, technological, and financial challenges. One of the key challenges will be a “safety assurance for hydrogen as a massive commercial product”. In previous hydrogen applications – in aviation, space, nuclear energy, process industries (oil/ gas/ chemical/ semiconductor/ metal/ glass/ food) – hydrogen safety was limited to the localized industrial sites, provided by dedicated industrial safety systems, operated by the trained personnel within organizations, committed to established industrial safety culture and the best safety practices. Hydrogen safety knowledge obtained, and experience mined earlier in the nuclear applications can be useful for development, design, maintenance, and assessment of safety of an emerging hydrogen energy infrastructure and hydrogen technologies (both upstream and downstream).

Report goal is to review the pros and cons of potential application of the Passive Autocatalytic Recombiners (PARs), developed for the nuclear power plants, in the emerging hydrogen energy and transport applications. In section 2 it is described a hydrogen safety problem, which is inherent to semi-confined or confined industrial, transport or residential spaces. In Section 3 the technological solutions – PARs, – developed during the last forty years for hydrogen safety provision of the nuclear power plants are briefly described. In section 4 the limitations of the current (second) generation of the hydrogen PARs are enumerated. In section 5 a need in third generation PARs is formulated. Innovative technology can be jointly developed by the process industry research and engineering communities in cooperation with nuclear communities to provide coming hydrogen energy infrastructure with a reliable, affordable, and inherently safe tool for hydrogen explosion prevention and mitigation.

Paper Received: 14 December 2021; Revised: 10 March 2022; Accepted: 10 May 2022
Please cite this article as: Kirillov I.A., 2022, Passive Autocatalytic Recombiners as Explosion Prevention and Mitigation Tool in Hydrogen Energy and Transport Infrastructures, Chemical Engineering Transactions, 90, 127-132 DOI:10.3303/CET2290022

2. Intrinsic problem of explosion safety in the hydrogen infrastructures

Now, one of the widely used and effective technical means for prevention and mitigation of the gaseous fuel-air explosions is a natural or forced (mechanical) ventilation of the semi-confined (tunnels, multi-storey outdoor parking structure, etc.) or confined (containments, hangars, underground indoor parking ramps, etc.) spaces within the industrial, energy and residential infrastructures.

However, investigations (see Figure 1) of the hydrogen incidents and severe accidents (in nuclear energy, in oil, gas and petrochemical industries) and focused lab-scale experiments (Grune, Sempert, Haberstroh, Kuznetsov, Jordan, 2013) resulted in understanding, that ventilation alone cannot provide total prevention or required mitigation of the hydrogen explosion risks.

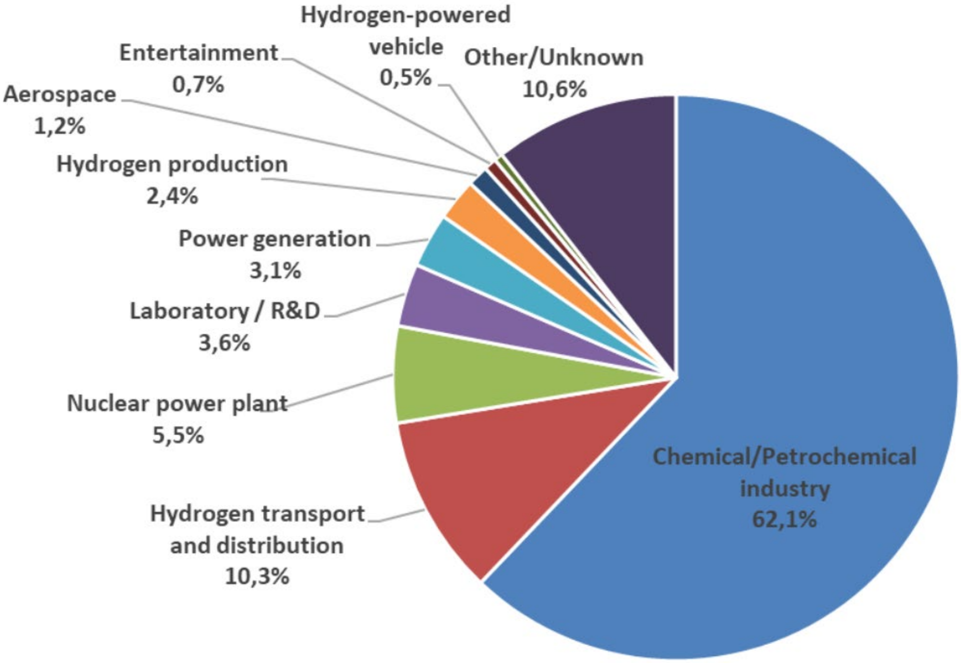


Figure 1: Percentages in different sectors in the hydrogen-related events (reproduction of Figure 6 from EHSP report, 2017)

Due to high buoyancy of hydrogen in atmosphere even in the ventilated structures there is possible a formation of the “dead corners” and/or the near-ceiling flat zones, where flammable hydrogen-air mixtures can be formed. Formation of the hydrogen-air mixtures, which cannot be eliminated by ventilation streams, may facilitate unacceptable consequences of the hydrogen-air combustion under accident conditions.

To cope with mentioned intrinsic problem of hydrogen safety the additional technical and technological means are required for the semi- and completely confined spaces in the future hydrogen infrastructures. Practical experience, knowledge, and technologies, developed in nuclear industry can be useful here.

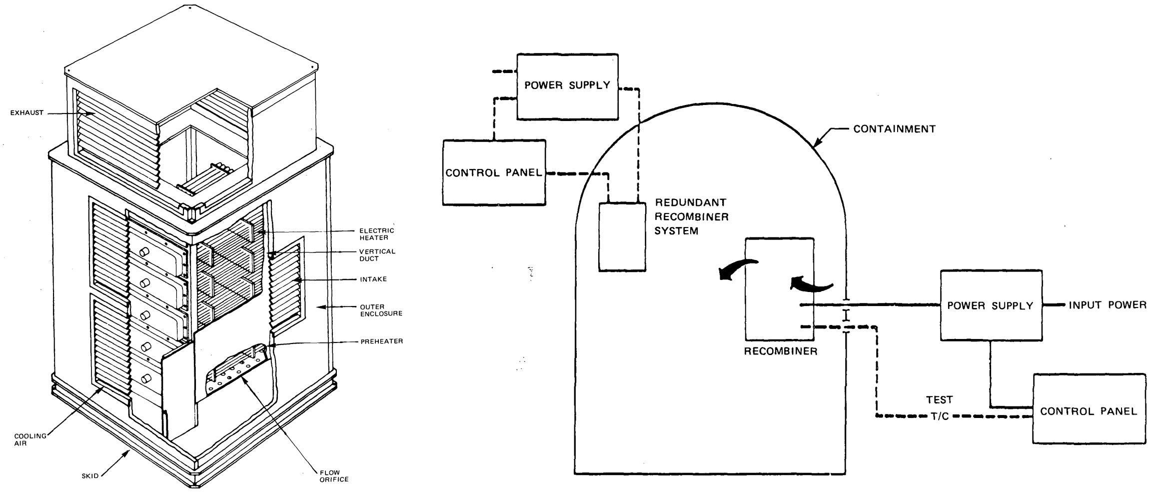
3. Passive Autocatalytic Recombiners (PARs)

Problem of hydrogen-air combustion and explosion prevention and mitigation has been in focus of nuclear industry from the 1950-th, when nuclear power plants (NPP) development and design started (Shapiro, Moffette, 1957). Nuclear reactors (PWR/VVER/CAMDU types) are mostly surrounded by the gas-tight containments (IAEA-TECDOC-1661, 2011), which can withstand the pressurization under severe accident conditions.

For safe removal of hydrogen from containment atmosphere under the Design Basis Accident (DBA) and Severe Accident (SA) conditions three classes of hydrogen recombiners were developed – flame, thermal and catalytic (Camp, Cummings, Sherman, Kupiec, Healy, Caplan, Sandhop, Saunders, 1983). “They differ primarily in the way that they initiate the recombination reaction. The thermal recombiner uses radiant heat to bring about recombination, while flame recombiners depend on a self-maintaining, exothermic combustion process. Catalytic recombiners use a noble metal catalyst bed to promote recombination at relatively low temperatures.”

Catalytic recombiners use catalysts (platinum, palladium, etc.) to oxidize (recombine) the hydrogen with oxygen in air at the gas/catalyst interface. Recombiners can operate outside the limits of flammability hydrogen-air gas mixtures. Two generic sub-classes of catalytic recombiners (IAEA-TECDOC-1661, 2011) have been developed and used at NPPs worldwide.

First generation of catalytic recombiners – so-called energy-dependent Thermal Recombiners (TR) (Camp, Cummings, Sherman, Kupiec, Healy, Caplan, Sandhop, Saunders, 1983) – was designed in the end of 1970-th specifically for the DBA conditions to operate either inside (Figure 2 left) or outside of containment. The powered gas pumps (Figure 2 right) delivered the containment atmosphere (hydrogen-air-steam-aerosols mixture) to heated catalysts.



a) b)

Figure 2: Typical design of inside-containment thermal hydrogen recombiner (left) and schematic of their power supply (right) (reproduction of Figure 4-46 and 4-47 from Camp et al., 1983)

Second generation – so-called energy-independent or Passive Autocatalytic Recombiners (PARs) - has been proposed and developed in the mid of 1980s (Della-Loggia, 1991).

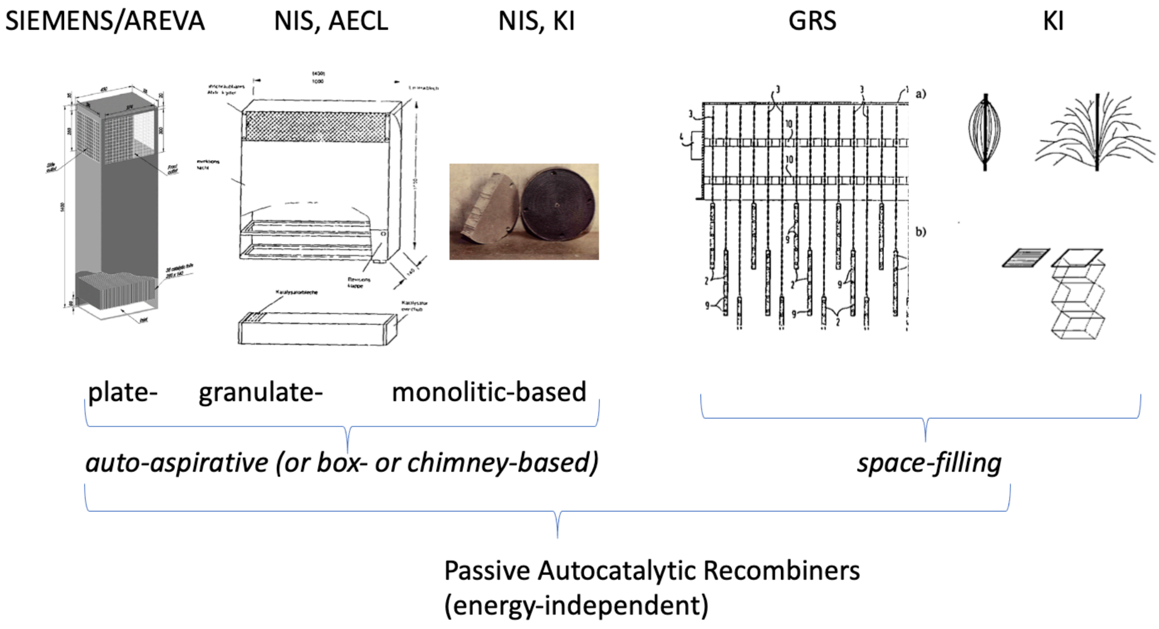


Figure 3: Basic designs of the PARs: “auto-aspirative” or “chimney-based” (left), “space-filling” (right).

In self-aspirating (or «box» or «chimney-based») PARs (Figure 3 left), which consist of catalyst surfaces arranged in an open-ended enclosure («chimney»), a catalytic reaction occurs spontaneously at the catalyst surfaces and the heat of reaction produces natural convection flow through the enclosure, exhausting the warm, humid hydrogen-depleted air and drawing fresh gas from below. Thus, the self-aspirating PARs do not need external power or operator action. Installation requires only to place PAR units at appropriate locations within the containment structures to obtain the desired coverage of the containment volume and the desired overall capacity. This PAR's capacities are ultimately subject to mass transfer limitations.

To cope with mentioned immanent limitation of the self-aspirating PARs three alternative designs (which can be named as "unfolded PARs" or "space-filling" recombiners) for enhanced catalytic hydrogen recombination have been proposed (Figure 3 right).

In Germany, Gesellschaft für Reaktorsicherheit (GRS) proposed and tested catalytic recombiners made by plasma injected Pd-Ni-Cu alloy on stainless steel plates in frame of a "Dual Concept" (or «German approach») (Rohde, Chakraborty, Huttermann, 1991). Plates were stacked in an inerted box to avoid contamination. Plates will be automatically unfolded and distributed through open space inside of containment for maximum catalysation.

In Soviet Union, Kurchatov Institute (KI) proposed a concept of "Controlled Recombination System" (Kirillov, Rusanov, Fridman, 1991). To overcome the hydrogen diffusion limitations and to avoid a formation of the "hot spots" it was proposed to use the ribbon (garland-like) or wire-based (dendrite-like) catalytic elements for organization of the catalytic structure with fractal dimension D_{fr} between 2 and 3.

Later in the second half of 1990s to reduce a risk of unintended ignition of the hydrogen-air mixtures by the "hot spots" at catalytic surface in self-aspirated PARs the THINCAT concept has been proposed (Fischer, Broeckerhoff, Ahlers, Gustavsson, Herranz, Polo, Roy, 2003).

All abovementioned catalytic recombiners were designed to operate in the following strategic combinations (IAEA-TECDOC-1661, 2011):

- Catalytic recombiners and igniters
- Catalytic recombination and post-CO_2 Injection
- Catalytic recombination and Containment Filtered Venting System (CFVS).

4. Pros and Cons for second generation PARs

4.1 Pros

Second-generation PARs were designed to ensure the hydrogen explosion safety of NPP units via two safety functions:

- to prevent or delay the formation of explosive hydrogen-air-steam mixtures inside of containment via flameless hydrogen recombination into water,

- to mitigate consequences of the potential hydrogen combustion via homogenization of the gas composition and temperature fields in the containment.

Existing PAR's can provide a stable rate of flameless hydrogen removal in a range of hydrogen concentrations (from ≈ 0.1 to ≈ 5,9–6 vol.%) [20-24], which is outside of the hydrogen-air flammability limits (4,1–75 vol.%).

PARs do not use an external energy source.

4.2 Cons

The heterogeneous nature of hydrogen oxidation in second-generation PARs results in the following disadvantages:

- low specific (per unit of the catalyst surface area) rate of hydrogen oxidation in comparison with the rate of hydrogen removal in the self-propagating flames. In the catalytic oxidation of hydrogen, the rate of hydrogen removal is proportional to the area of the interface between the catalyst and steam-hydrogen-air gas mixture and is limited by hydrogen and/or oxygen diffusion from gas mixture volume to catalytic surface,

- the formation of "hot spots" on the catalyst surface and, consequently, the local initiation of combustion waves ("flames") that can independently (without the action of the catalyst) propagate through the gas mixture inside and outside the PAR. Spontaneous formation of "hot spots" on the catalyst surface occurs due to spatial heterogeneity in the distribution of atomic centers of catalytic activity at the interface and can, in principle, be technologically controlled or excluded. In available PARs the "hot spots" formation (Meynet, Bentaib, 2010) results in uncontrolled "catalytic ignition", which manifests itself through two possible mechanisms (Kharitonova, Kirillov, Bezgodov, Simonenko, 2014):

• "internal mechanism" - the formation of a self-sustaining flame near the "hot spots" of the catalyst, its propagation inside the PAR, leaving the PAR casing and further spreading independently of the processes inside the PAR. The result of the formation of "hot spots" on the catalyst surface is the local initiation of combustion waves ("flames"), independently (without the action of the catalyst) propagating through the gas mixture inside and outside the PARs housing,

• “external mechanism” - detachment of the catalytic particles from the metallic or ceramic substrate, its removal outside the PARs casing, entering the area, in which the concentration and temperature are sufficient for catalytic self-heating of an individual particle.

Potential safety problems, associated with the “catalytic ignition” phenomenon, which was recorded for all commercially available second-generation PARs under severe accident conditions, forcing development of the third generation of the PAR with inherently safe design.

5. Inherently safe third generation PARs

Development, production and standardization of the third generation PARs with inherently safe design, which prevent formation of the “hot spots” at catalytic surface, is important for two large R&D communities – in nuclear energy and in process industries.

First ones have an ample practical experience with the PARs, aimed to reduce risks of the hydrogen explosions (detonative or deflagrative).

Second ones possess comprehensive capabilities in development of the catalysts with required characteristics and optimization of the catalyst-based hardware and technologies.

Cooperation between the mentioned communities can be beneficial for hydrogen explosion risk and resilience management both in matured nuclear energy and in emerging hydrogen-energy and transport infrastructures.

6. Conclusions

1. Practical implementation and social acceptance of the hydrogen energy and transport infrastructures will be equally defined by their technological advancement, cost, and safety level in comparison with the carbon-based ones.
2. Safety of the critical components of hydrogen energy and transport – tunnels, underground and multi-storey parkings, industrial structures for hydrogen production/distribution/storage – is defined both by size of accidental hydrogen leaks/spills and degree of confinement and/or congestion of space, where accident occur. Even in the ventilated (naturally or forced) compartments the “dead corners” or the near-ceiling zones exists, where flammable hydrogen-air mixtures can be formed and can result in unacceptable consequences under accident conditions.
3. Two generations of the catalytic recombiners have been developed and are now widely used inside of the totally confined containments of the basic types of the nuclear power plants (PWR, VVER, CANDU). Pros and cons of the Passive Autocatalytic Recombiners are briefly described. Flameless hydrogen recombination by the second-generation PARs occurs within a limited range of the hydrogen-air mixture stoichiometry. Outside of this concentration range technical control of the PAR-induced flames is hindered.
4. Self-intake (or chimney-based) PARs can potentially be useful for hydrogen explosion safety provision of the semi-confined or confined structures inside of the hydrogen energy and transport infrastructures.
5. Substantial reduction of the hydrogen explosion risks in can be achieved by a prospective third generation inherently safe PARs, where volumetric ignition of the hydrogen-air mixture by catalytic surface is excluded.
6. Joint technological development of a third generation of PARs (inherently safe) can be effectively made via collaboration of the research and engineering communities in the process industries and in the nuclear energy.
7. Now generally accepted international standards on PAR’s performance and safety margins are absent. Standardization of the third-generation PARs by the appropriate international bodies can be valuable and effective step for a global hydrogen energy and transport promotion and acceptance.

Acknowledgments

Author is grateful to Hans Pasman (NL) and Vadim Simonenko (RU) for encouraging discussions and multiple advices.

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