DESIGN OF CATALYTIC RECOMBINERS FOR SAFE REMOVAL OF HYDROGEN FROM FLAMMABLE GAS MIXTURES

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ABSTRACT

Several today's and future applications in energy technology bear the risk of the formation of flammable hydrogen/air mixtures either due to the direct use of hydrogen or due to hydrogen appearing as a by-product. If there's the possibility of hydrogen being released accidentally into closed areas countermeasures have to be implemented in order to mitigate the threat of an explosion. In the field of nuclear safety passive auto-catalytic recombiners (PAR) are well-known devices for reducing the risk of a hydrogen detonation in a nuclear power plant in the course of a severe accident. Hydrogen and oxygen react on catalyst materials like platinum or palladium already far below conventional flammability limits. The most important concern with regard to the utilization of hydrogen recombiners is the adequate removal of the reaction heat. Already low hydrogen concentrations may increase the system temperature beyond the self-ignition limit of hydrogen/air mixtures and may lead to an unintended ignition on hot parts of the PAR.

Starting from the nuclear application, since several years IEF-6 and LRST perform joint research in the field of passive auto-catalytic recombiners including experimental studies, modeling and development of new design concepts. Recently, approaches on specifically designed catalysts and on passive cooling devices have been successfully tested. In a design study both approaches are combined in order to provide means for efficient and safe removal of hydrogen. The paper summarizes results achieved so far and possible designs for future applications.

1.0 INTRODUCTION

Today hydrogen is used in many industrial applications. Its handling is restricted to skilled staff in specially designed processes and areas. In the near future, with increasing introduction of hydrogen into everyday life in terms of e.g. fuel cells and hydrogen powered cars, there is a large number of applications to be expected outside specifically designated areas and used by untrained people. This progression means a great challenge with regard to the safety design of products and applications.

Moreover, the increasing number of hydrogen technologies will lead to numerous applications which bear the risk of the formation of flammable hydrogen/air mixtures either due to the direct use of hydrogen or due to hydrogen appearing as a by-product. If there's the possibility of hydrogen being released accidentally into closed areas countermeasures have to be implemented in order to mitigate the threat of an explosion. Especially when considering the public acceptance of hydrogen as a future energy carrier, safety devices for avoiding such threats will play an important role. While today most industrial applications avoid or control flammable mixtures the most common mitigation strategy is to dilute the mixture by appropriate venting. However, some applications remain where venting has its limits: fuel cell or hydrogen powered cars are the most prominent amongst numerous examples for future applications of hydrogen that will be associated with closed and semi-closed areas like garages, tunnels etc.

2.0 CATALYTIC RECOMBINERS

In the field of nuclear safety passive auto-catalytic recombiners (PAR) are well-known devices for reducing the risk of a hydrogen detonation in a nuclear power plant (NPP) in the course of a severe accident [1]. As a consequence of chemical reactions during the core-melt sequence hydrogen is released into the containment forming a gaseous mixture with air. PAR boxes (Fig. 1) distributed inside the reactor containment of the NPP convert the hydrogen into steam and heat by means of catalytic recombination. Hydrogen and oxygen react on catalyst materials like platinum or palladium already far below conventional flammability limits.

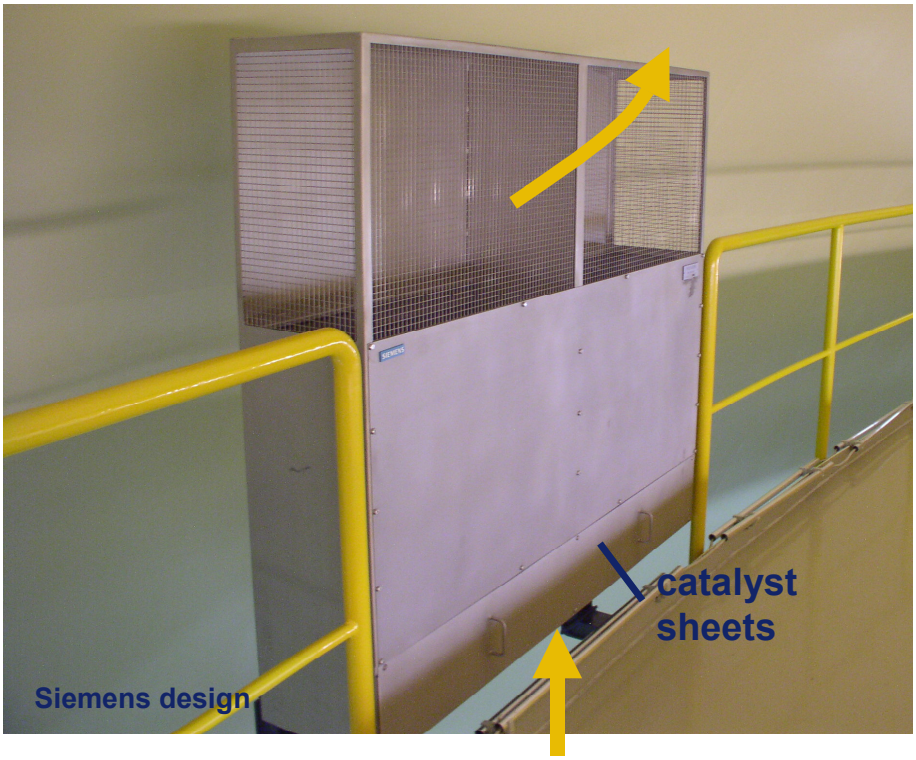

Figure 1. PAR installed inside a nuclear power plant

The conversion of hydrogen into harmless steam by means of catalytic recombination represents a measure that may be used complementary to a venting strategy or as a stand-alone measure. In case of a natural convection driven PAR (Fig. 2, left) the hydrogen-rich gas mixture enters the recombiner box through the bottom opening and passes through rectangular flow channels formed by catalytic coated steel sheets. The exothermal reaction is activated already at low (ambient) temperatures and below conventional flammable mixtures converting hydrogen into harmless steam and heat (~240 kJ/mol). The resulting buoyancy effect drives the gas through the chimney and out of the top opening enabling the feed of fresh gas from the environment. The outlet opening is located at the box front and protected by a wire mesh in order to avoid ingress of interfering particles. Recombiners designed for application under forced flow conditions (Fig. 2, right) may be integrated e.g. in pipe lines.

The PAR is a fully passive acting system, i.e. no additional external power supply or operational action is necessary in order to start and support the operation. A proper location of a sufficient number of PAR allows for prevention of the formation of flammable mixtures inside the enclosure without additional venting devices. However, in general a PAR represents a safety measure that may be used complementary to other techniques, e.g. venting or inerting, as the demands on PAR for non-nuclear applications can be quite different. With an increasing number of hydrogen applications numerous

different scenarios with regard to possible release amount and rates, flow and process conditions etc. have to be considered. PAR designs will have to reflect the respective boundary conditions.

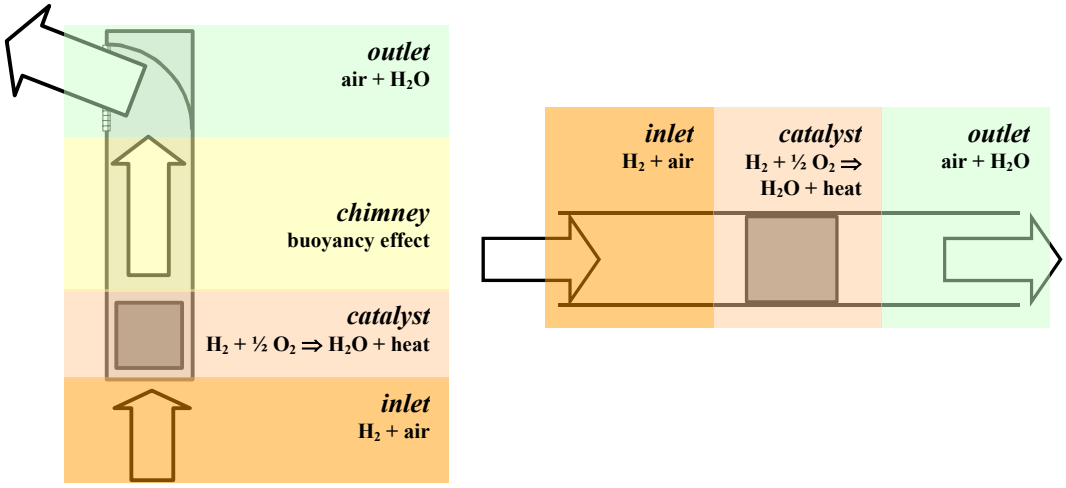

Figure 2. Principle of a passive auto-catalytic recombiner (PAR) for natural convection (left) and forced flow conditions (right)

The major drawback of today's PAR designs is the possible ignition of the hydrogen-rich mixture on the hot catalyst sheets. Already low hydrogen concentrations may increase the local temperature close to the leading edge of the catalyst sheet beyond the self-ignition limit of hydrogen/air mixtures (~560°C) and may lead to an unintended ignition. Measurements performed at IEF-6 reveal that, depending on the catalyst element design, already at concentrations as low as 4 vol.% the conventional ignition temperature is reached (Fig. 3). While hydrogen concentrations are further increasing the probability of an unintended ignition grows.

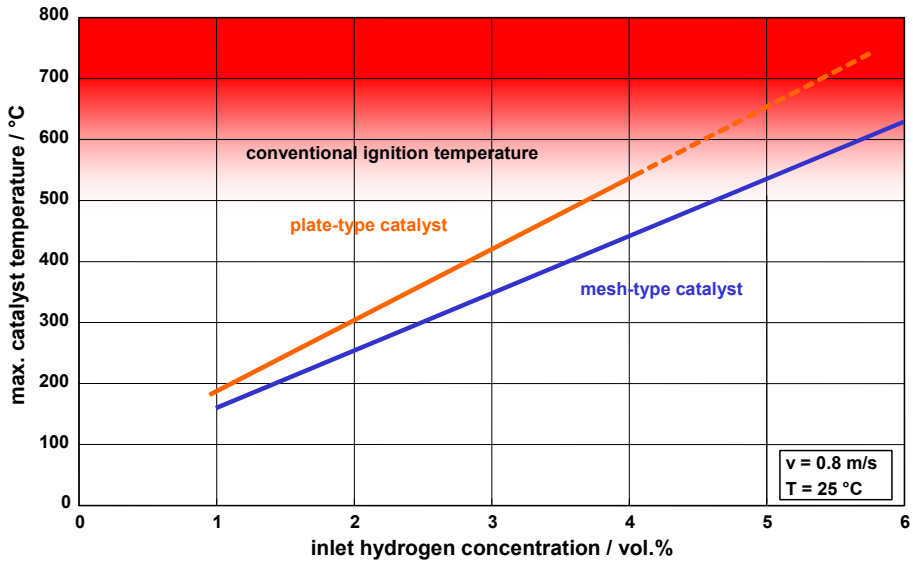

Figure 3. Maximum catalyst temperature as a function of the inlet hydrogen concentration for different catalyst element types: a) catalyst sheets, b) catalyst meshes

Consequently, the most demanding challenge for PAR designs is the passive system temperature control. This is not a trivial task in connection with a passive device where measures like active cooling or inlet mixture control are not at disposal. Furthermore, the catalyst needs to be designed for resistance against poisoning and related environmental influences, which may however vary strongly from the application.

3.0 DESIGN STUDIES

The challenge to realize an efficient hydrogen removal with sufficient limitation of the catalyst temperatures in order to avoid ignition demands a strategy for controlling the heat generation (exothermal reaction) as well as for the heat removal. Two general approaches have been investigated:

- local limitation of the catalytic reaction
- passive cooling of the catalyst elements

Local limitation of the catalytic reaction may be achieved either by the composition of the catalyst or by the geometrical design of the support. Passive cooling of the catalyst elements may be as well achieved either by geometrical design or by additional cooling measures.

Three basic element types of combined catalyst and support have been identified, characterized by both their support and catalyst design:

- high performance catalyst - large surface elements (HPC-LS)
- adapted performance catalyst - large surface elements (APC-LS)
- high performance catalyst - passive cooling elements (HPC-PC)

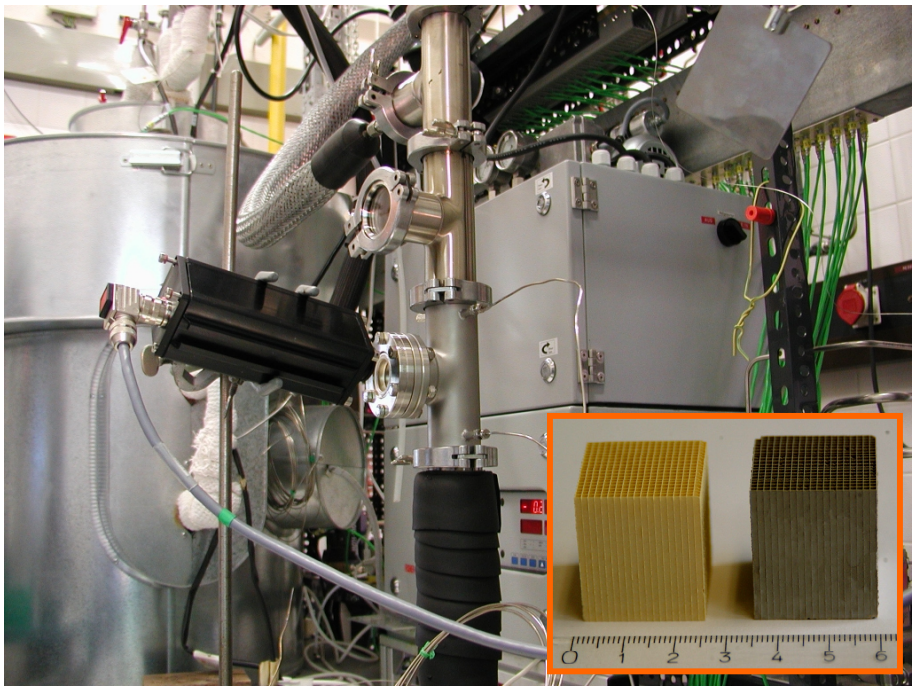

Figure 4. REKO-1 facility for testing of catalyst samples [2]

Experimental research has been performed studying the operational behavior of these different designs under well defined conditions. For this purpose, the REKO-1 (Fig. 4) and REKO-3 facilities have been established as test facilities for the evaluation of the conversion efficiency and thermal characteristics of catalyst elements for hydrogen recombination [3]. The catalyst elements are located inside the vertical flow channel of the facilities. Well defined conditions with regard to flow rate, inlet gas composition and gas temperature are applied. Catalyst temperatures, gas temperatures and the gas composition along the catalyst sheets are the essential measurements as the gas mixture (hydrogen, air, nitrogen, steam) passes the catalyst samples. Besides information on the thermal behavior and ignition potential the results yield data on the PAR efficiency as well as data on the reaction kinetics. Related to the experimental studies, the recombiner simulation REKO-DIREKT has been developed as a tool capable of modeling the local thermal behavior of a recombiner as well as the hydrogen conversion along the catalyst elements. The code has been validated against the data base available from the REKO experiments.

An efficient catalyst element can be realized using a common washcoat-based catalytic coating on steel wire mesh samples as substrate material (HPC-LS). The conversion rate (and the catalyst temperature accordingly) increases linear with the inlet hydrogen concentration (Fig. 5). Consequently, an ignition at elevated concentrations is inevitable. Adapting the conversion capacity (APC-LS) - in the study performed [4] by means of an electroplated coating - limits the maximum conversion rate and the maximum catalyst temperature as well. In the present case, the full gas mixture range could be applied without ignition of the gas mixture. Mixtures above 22 vol.% hydrogen were not reactive in the presence of the catalyst samples due to oxygen deficiency.

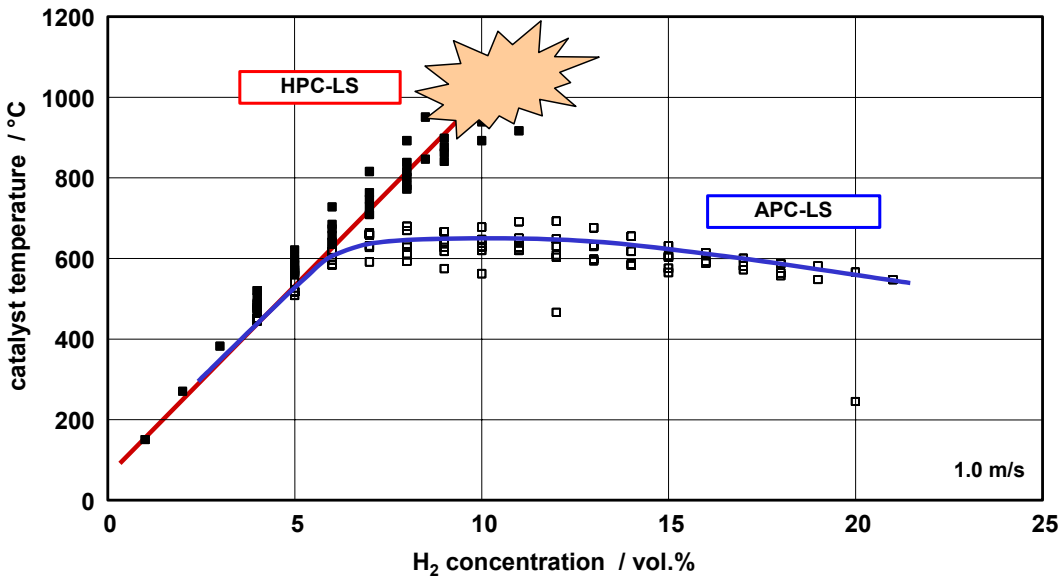

Figure 5. Catalyst temperature vs. the hydrogen concentration
with different catalyst designs

In order to avoid an over-limitation of the catalyst activity which may lead to an increased sensitivity against catalyst poisoning, passive cooling is an additional measure to be applied. Fig. 6 shows measurement results for the successful combination of catalyst and heat pipe (HPC-PC). The catalyst has been applied to the hot end of the heat pipe. Compared to the reference case - a steel substrate of the same geometry as the heat pipe - the catalyst temperature is efficiently reduced to values far below the ignition temperature [5].

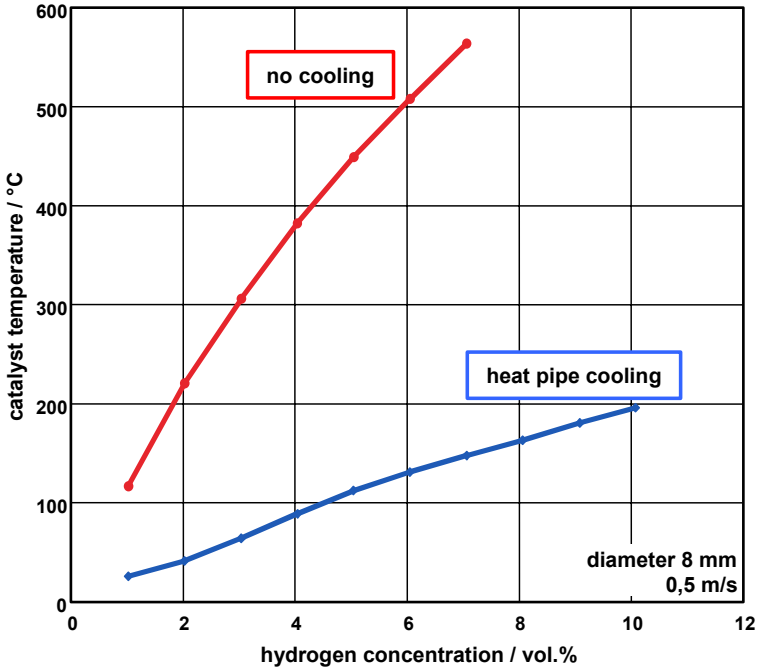

Figure 6. Passive catalyst cooling with heat pipes (HPC-PC)

A new enhanced APC-LS design consists of a catalyst based on Pt-nano-particles embedded inside a metal oxide matrix. This catalyst has been successfully applied to different substrate materials. On ceramic cells (Fig. 4, small picture) high efficiencies are achieved with a limited maximum temperature of about 450°C (Fig. 7).

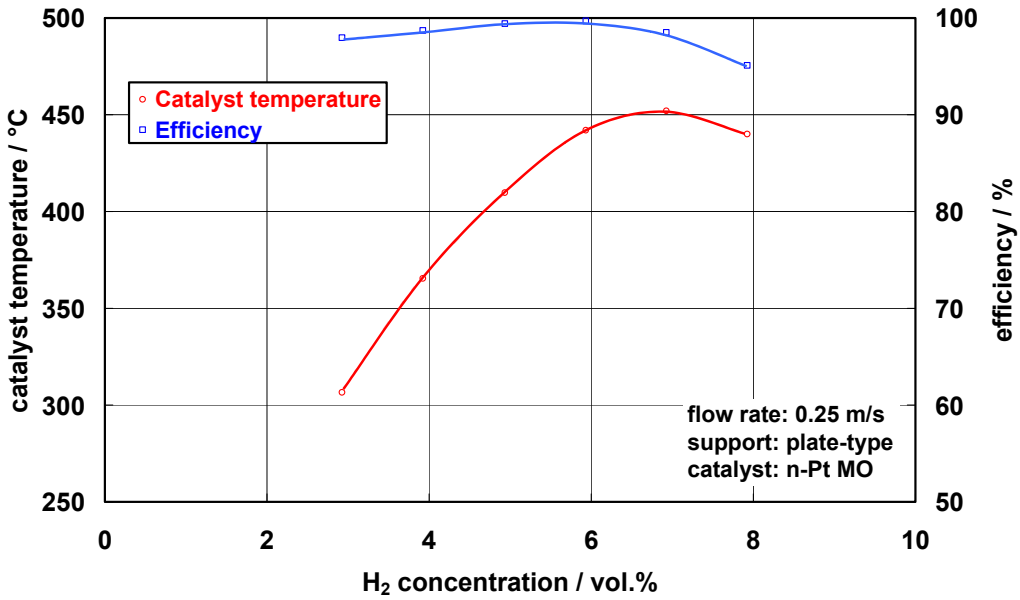

Figure 7. Catalyst temperature and conversion efficiency as a function of the inlet hydrogen concentration with enhanced catalyst design (APC-LS)

The basic features of these three designs are summarised in Table 1. It has to be stressed that the numbers given are highly dependent on parameters e.g. flow rate, hydrogen concentration, support design, and serve only as a rough orientation.

Table 1. Overview of the basic features of the different catalyst designs investigated

type	catalyst	support	start behaviour	efficiency / element	thermal behaviour
HPC-LS	**high performance**	**large surface**	**~ 2 vol.%**	**~ 70 %**	**unlimited heating up**
APC-LS	**adapted performance**	**large surface**	**< 1 vol.%**	**> 90 %**	**limited to ~ 450°C**
HPC-PC	**high performance**	**passive cooling**	**~ 2 vol.%**	**~ 10 %**	**limited to ~ 200°C**

In a modular set-up the different approaches may be combined according to the relevant acceptable temperature ranges and design requirements of the application. Fig. 8 shows a design for a low hydrogen concentration scenario (e.g. 5 vol.%) that may be mitigated by a HPC recombiner as long as temperatures of ~ 500°C are acceptable at the recombiner outlet. For these conditions, efficient hydrogen removal may be realized in a compact design layout.

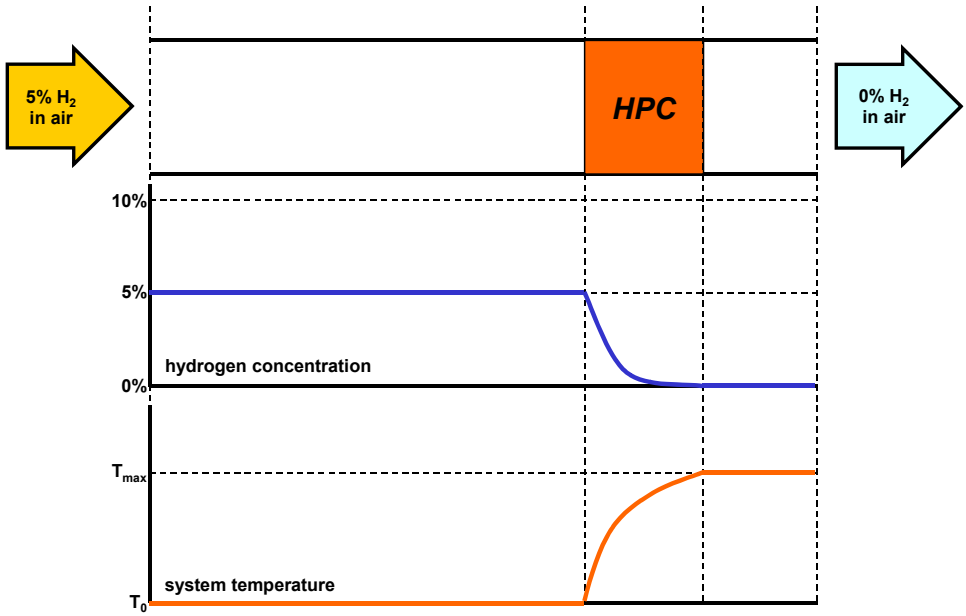

Figure 8. Modular PAR, medium inlet H_2 concentration

If the outlet temperature has a lower acceptance level a cooling module combined with the HPC element may become necessary (Fig. 9). Depending on the application this module can be designed passive or supported by an active device.

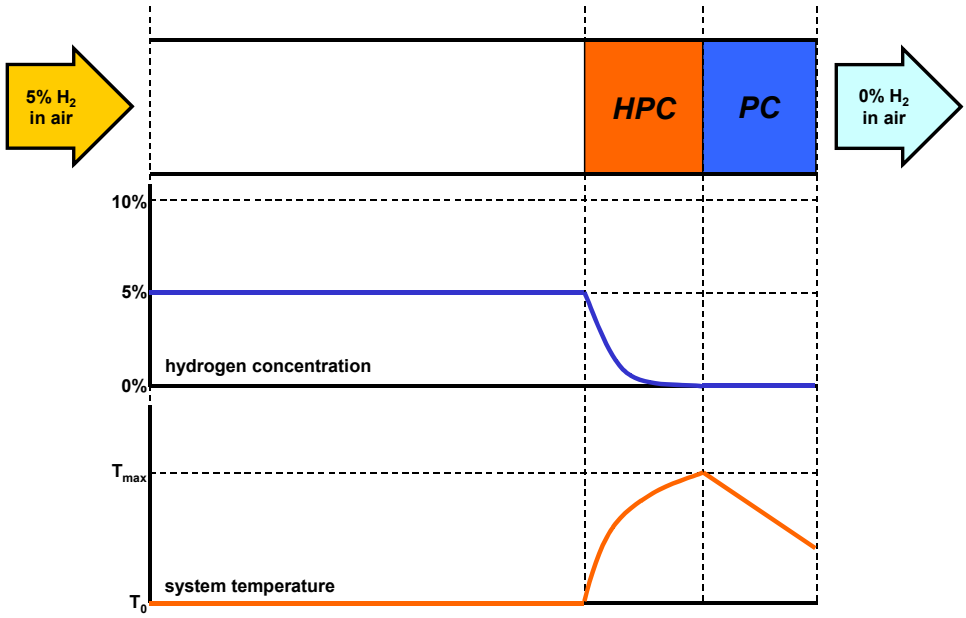

Figure 9. Modular PAR, medium inlet H_2 concentration, low outlet temperature

For high amounts of hydrogen, e.g. 10 vol.% and above, a first APC recombiner stage is inevitable. Application of APC as shown in Fig. 10 can reduce the hydrogen concentration to a level acceptable for HPC. The HPC element enables efficient depletion down to the desired level.

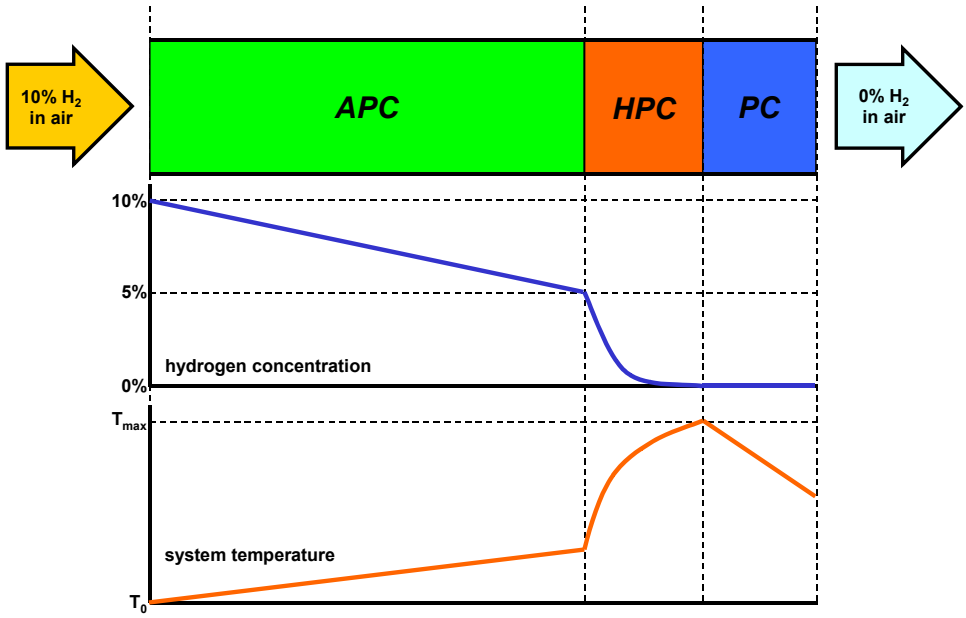

Figure 10. Modular PAR, high inlet H_2 concentration, low outlet temperature

4.0 CONCLUSIONS

Although catalytic recombiners are generally available from the application in nuclear power plants some important drawbacks exist hindering the application as a safety measure in hydrogen applications. Most challenging is the optimum layout of the catalyst section providing efficient hydrogen removal while maintaining the system temperature well below the ignition limit. Different approaches have been studied taking into account optimised catalyst designs as well as passive cooling devices. Both approaches - conversion limitation and passive cooling - can be combined in a modular way combining the advantages of both approaches and enabling the adaptation to the corresponding requirements. For the near future, the realisation of a combined concept in a prototype is planned.

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