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Impact of oxygen starvation on operation and potential gas-phase ignition of passive auto-catalytic recombiners

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ABSTRACT

A large amount of hydrogen can be released into the containment of light water reactors during a severe accident. Passive Auto-catalytic Recombiners (PARs) aim to avoid flame acceleration and excessive pressure loads on the containment in case of hydrogen combustion. Their operation is based on the catalytic recombination of hydrogen into steam in the presence of oxygen. Thus, the recombiners reduce the hydrogen but also the oxygen content in the containment atmosphere. As a consequence, the oxygen/nitrogen ratio diverts more and more from the standard 21 vol.% in air. This decreasing ratio may impact on the PAR efficiency. Additionally, the exothermic surface chemical mechanism leads to the overheating of the catalytic plates and activates the natural convection inside the recombiners. This heat source can also create local conditions for hydrogen combustion in the gas phase, as igniters do. Hence, the oxygen/nitrogen ratio may also determine the conditions for the gas-phase ignition inside PARs. This study deals with the numerical simulation of the impact of the oxygen starvation (i.e. low oxygen/nitrogen ratio) on the PAR efficiency and on the PAR gas-phase ignition limit. Calculations are performed with a dedicated CFD code named SPARK. We focus on the interaction of recombiners with any $H_2/O_2/N_2/H_2O$ mixtures and thus establish a quite complete understanding of PAR operation. Calculations confirm the experimental oxygen surplus (i.e. twice more oxygen than stoichiometry) necessary to ensure an optimal PAR efficiency ($X_{O_2} \approx X_{H_2}$) independently of the steam content. The PAR gas-phase ignition limit is then determined numerically in the classical H_2/Air/H_2O ternary diagram with a very good agreement with the available experimental database. It points out the importance of catalyst heat radiation, and more secondarily of species thermal diffusion (i.e. Soret effect). Finally, the PAR gas-phase ignition limit is determined for all oxygen/nitrogen ratios. The ignition domain appears to strongly contract when the oxygen content decreases, so that the steam threshold for inertization of the containment with respect to the recombiners ignition becomes very low.

1. Introduction

In case of a severe accident (SA) in light water reactors, a large amount of hydrogen (H_2) can be released into the containment firstly during the early phase of zircaloy cladding oxidation in the reactor vessel and secondly together with CO and CO_2 during the late phase of interaction between molten corium and concrete (MCCI) after the vessel rupture. Depending on the convective mixing of the containment atmosphere, hydrogen may exceed the flammability limit and so threaten the integrity of the containment in case of combustion. To mitigate the hydrogen risk related to flame acceleration or excessive pressure loads on the containment in case of combustion, French pressurized water reactors (PWRs) combine a large free volume to enhance atmosphere dilution, a high value of the containment design pressure and Passive Auto-catalytic Recombiners (PARs) to consume hydrogen.

PARs are usually designed using row of vertical catalytic plates with platinum and palladium on ceramic washcoat housed inside a metallic structure (cf. Fig. 1). Their operation is based on the catalytic recombination of hydrogen into steam in presence of oxygen:

$$2H_2 + O_2 \rightarrow 2H_2O + 242\ \text{kJ/mol}. \quad (1)$$

During SA, the oxygen content in the containment atmosphere decreases, as a consequence of the PAR operation. Hence, the oxygen/nitrogen ratio does not match the standard 21 vol.% in air. Therefore, a low oxygen/nitrogen ratio may impact on the

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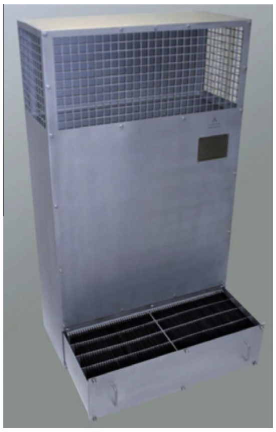

Fig. 1. Example of passive autocatalytic recombiner (AREVA PAR FR1-380T).

PAR efficiency. Additionally, the exothermic surface chemical mechanism leads to the overheating of the catalytic plates and activates natural convection driven circulation of gases in contact with the catalyst. This heat source induced by the PAR operation can also create local conditions for hydrogen gaseous combustion, as igniters do [1]. Therefore, the oxygen/nitrogen ratio may also determine the conditions for the PAR gas-phase ignition.

The decision of nuclear safety authorities to implement PARs in nuclear power plants has been supported by several experimental programs which were initially focused on the general performances of the catalytic recombiners and their mixing behavior. Then, PARs have been tested under conditions representative of SA environments with steam, oxygen starvation, radioactive or chemical poisoning and also gas-phase ignition. A wide experimental database for recombiners was therefore obtained, and more generally for catalytic reactors, among which the most recent experiments are: H2PAR and PHEBUS programs at IRSN [2,3], KALI-H2 program at CEA [4], OECD/THAI program at Becker Technologies [5], REKO program at Forschungszentrum Jülich [6] and OECD/SETH-2 program at the Nuclear Energy Laboratory of Paul Scherrer Institute (PSI) [7]. Experiments with catalytic reactors for H_2 power generation at the Combustion Laboratory of PSI [8,9] completes this database for a detailed insight in catalytic ignition phenomena. In parallel, the effort about PARs modeling has led to a variety of models from empirical correlations given by the manufacturers [10] to mechanistic models [11–13] and detailed CFD calculations. Each modeling has its specific range of applications regarding the type of recombiners, operating conditions, accident scenarios or physical issues. Although CFD models are the most suitable for complex geometries and/or chemical kinetics related phenomena, they are generally used to study PAR operation at standard conditions of pressure and temperature and low hydrogen contents. For this kind of application, global chemistry and detailed chemistry modeling of the catalytic surface give equivalent results with respect to experimental measurements of hydrogen conversion and catalyst temperature [11,14–16]. CFD approaches with global chemistry are also used to compute full catalytic set-up [15,17] and so justify the reduced numerical domain often considered with detailed chemistry modeling, or to evaluate the PARs efficiency at removing hydrogen inside realistic configurations [18]. CFD calculations with detailed chemistry modeling of the catalytic and gas-phase mechanisms occurring inside the recombiners were recently performed to study the PAR gas-phase ignition with H_2/Air mixtures [19].

This study deals with numerical simulation of the impact of oxygen starvation on the efficiency of operating PARs inside PWRs, but also on their gas-phase ignition limit. The physical modeling of the PAR operation under oxygen starvation was addressed with the lab-scale facility REKO-3 at Jülich [20], and in the frame of the PHEBUS program but for catalytic coupons not directly representative of PAR operation [21]. In this study, calculations are performed by using a dedicated code named SPARK which is currently developed at IRSN [19] and considering real dimensions of the catalytic section inside a recombiner. This numerical tool is based on the detailed physical modeling of multicomponent transport, gas phase/surface chemistry, and surface heat radiation, inside a recombiner. This CFD code aims at studying surface related phenomena as PAR gas-phase ignition, PAR efficiency under oxygen starvation, PAR interaction with carbon monoxide (CO) or PAR interaction with CsI aerosols. SPARK has been intensively validated for PARs and catalytic reactors operating with $H_2/O_2/N_2/H_2O$ mixtures [11,16,19,21], but also with CO and CO_2, over the aforementioned experimental database [17].

In this work, we focus on the interaction of recombiners with any $H_2/O_2/N_2/H_2O$ mixtures, and so establish a map of PAR efficiency. Calculations first concern the impact of oxygen starvation (i.e. low oxygen/nitrogen ratio) in the absence of steam on the PAR efficiency and on their potential gas-phase ignition. A minimum oxygen surplus to ensure the PAR efficiency is determined for mixtures with and without steam. Then, the PAR gas-phase ignition limit is validated in the classical H_2/Air/H_2O ternary diagram and extended to several dilution ratios. Finally, a steam threshold for the inertization of the containment atmosphere with respect to the PAR gas-phase ignition is evaluated.

2. The “SPARK” code

The SPARK (Simulation for Passive Autocatalytic Recombiners’ risK) code is a dedicated numerical tool developed at IRSN for catalytic reactor-type applications. It solves the two-dimensional steady-state Navier–Stokes equations in the vorticity–velocity formulation by including detailed gas-phase and surface chemistry, multi-component transport, and heat radiation [19].

2.1. Numerical domain

The numerical domain is derived from the box-type PARs with row of vertical catalytic sheets as illustrated in Fig. 2. We suppose very thin catalytic plates, so that the horizontal solid heat conduction is neglected. Transverse heat conduction from the catalytic sheets to metallic box, and external heat convection, are not taken into account. The latter are negligible for the catalytic sheets located in the middle of the PAR which are consequently the hottest sheets. Their study ensures a conservative evaluation of the PAR gas-phase ignition risk within the framework of the nuclear safety. Then, the flow can be supposed to be symmetrical and the numerical domain is reduced to a half-channel between two catalytic plates in the median plane of the recombiner (cf. Fig. 2). Also, for the typical PARs operating conditions, the Reynolds number Re_{4h} remains below 2300 so that the flow can be considered laminar.

2.2. Governing equations

The governing equations are based on the modified vorticity-velocity formulation of the Navier–Stokes equations for two-dimensional planar reactive flows [22]. The gas-phase equations are written as follows:

- Horizontal velocity:

$$\partial^2_{xx} u + \partial^2_{yy} u = \partial_y \omega - \partial_x\left(\frac{u}{\rho}\partial_x \rho + \frac{v}{\rho}\partial_y \rho\right), \qquad (2)$$