OPERATIONAL BEHAVIOUR OF CATALYTIC RECOMBINERS – EXPERIMENTAL RESULTS AND MODELLING APPROACHES

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Abstract

Autocatalytic passive recombiners (PAR) are implemented in containments as an accident management measure to mitigate the consequences of possible hydrogen combustion in the course of a severe accident. The performance of a PAR has been demonstrated in large scale tests; however these integral tests provided no data for detailed model development. At Forschungszentrum Jülich separate effect tests are performed in order to obtain experimental data suited for the validation of detailed numerical models for the assessment of the operational behaviour of PAR. The paper describes the experimental facilities and results obtained so far.

Two modelling strategies are pursued and assessed with their applicability and further development needs. The detailed evaluation of the reaction kinetics and heat and mass transport phenomena on a single catalyst element is performed by a direct implementation of the transport and kinetic approaches in ANSYS CFX 11. To model the interaction of PAR with the containment and address the issues mentioned above, REKO-Direkt, a detailed user model based on Fortran 90 will be implemented in CFX to model the entire PAR. This in-house code is already validated against the database and capable to model all relevant processes. Finally some results of local interaction studies are presented.

1 INTRODUCTION

The nuclear safety is based on the "defence-in-depth" concept, introduced by the International Atomic Energy Agency (IAEA, 1996). This concept consists of hierarchical levels of equipment and procedures to preserve the integrity of the physical barriers.

During severe accidents (SA) in light water reactors, hydrogen is generated by the exothermal oxidation of the fuel claddings, hot metallic components and after failure of the reactor pressure vessel and melt relocation to the reactor pit due to decomposition of concrete as well. These processes produce hydrogen with such high rates and for a long term in the course of a SA that the local volumetric concentrations inside the containment exceed the lower flammability limit. Both major nuclear accidents of Three Mile Island (TMI) in 1979 and Chernobyl in 1986 resulted in a world-wide investigation of SA and the hydrogen risk.

The protection of the containment against the consequences of a hydrogen deflagration or even explosion is an integral part of the forth level *("...prevention of accident progression and mitigation of the consequences of severe accidents…")*. Due to the relative small containment size of boiling water reactors (BWR) the atmosphere is diluted or even inerted with nitrogen or carbon dioxide in order to prevent combustible hydrogen mixtures. In an increasing number of European pressurized water reactors (PWR) the containment has been refitted with passive auto-catalytic recombiners (PAR) as an accident management measure. Hydrogen and oxygen react exothermally on the catalytic surfaces inside a PAR generating steam and heat beyond conventional flammability limits (Bachellerie et al., 2003). The reaction heat creates a buoyancy driven flow which makes a PAR a completely passive operating device. Present commercially available and implemented PAR designs are box-type PAR of AREVA (France/Germany) and Atomic Energy Canady Limited (AECL, Canada) and porous bed type PAR of NIS Company (Germany). Figure 1.1 shows a PAR of AREVA design, mainly back fitted to European PWR containments, and a section of the catalyst sheets.

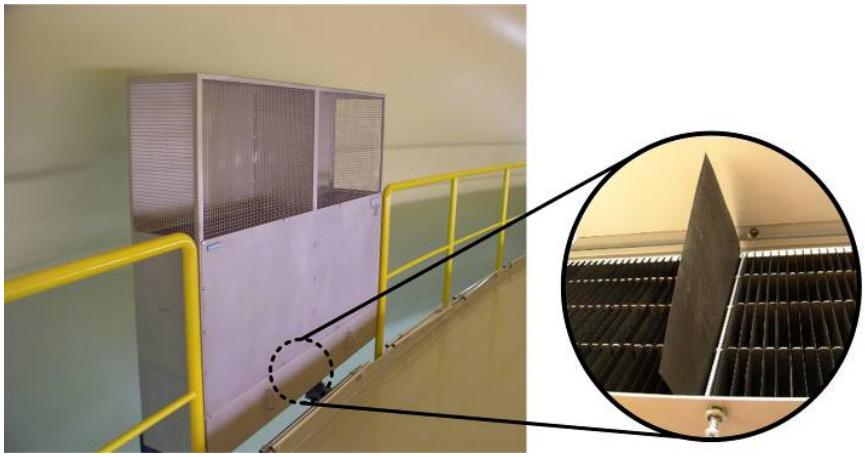


Figure 1.1: AREVA-design PAR: Implementation and detailed view on catalyst section

In the frame of SA analysis reliable numerical models are a vital element for the assessment of PAR performance and efficiency in accident scenarios. International research activities e.g. in the European FP-6 Network of Excellence SARNET (Severe Accident Research NETwork) investigate related aspects. The important modelling issues are on the one hand the phenomena inside the PAR, e.g. the buoyancy driven flow and hydrogen depletion due to the catalytic surface reaction. On the other hand, the interaction with the containment atmosphere in particular the PAR outflow and its influence on the mixing process, the inducing of natural convection by the hot PAR box housing, and the effect of forced flow conditions are addressed. Safety related criteria such as possible gas-phase ignitions caused by hot parts due to the exothermal reaction are considered as well.

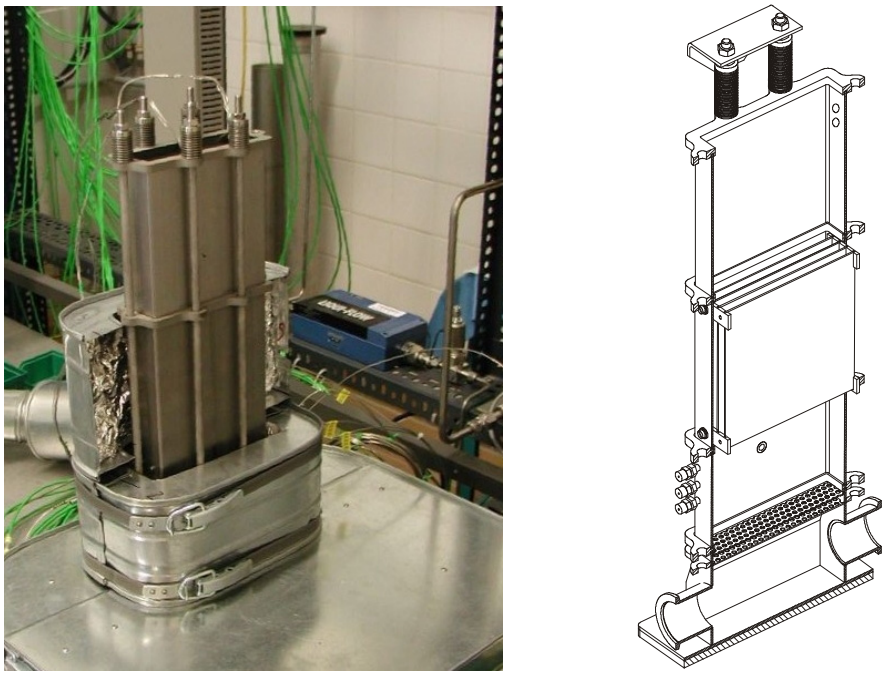
Numerous integral experiments have been performed in the past aiming at demonstrating the PAR performance under realistic conditions. However, developing detailed numerical models from these integral and mostly transient data represents a difficult if not impossible task leading to “black-box” models which have a limited application range and do not cover all relevant parameters to sufficiently deal with the above-mentioned issues.

2 EXPERIMENTAL STUDIES

In order to fill existing knowledge gaps and complement the existing data base, detailed experiments are performed at the Institute for Safety Research and Reactor Technology (IEF-6) at Jülich. In the small-scale test facility REKO-3, representing a recombiner section, detailed investigations of the reaction kinetics under well-defined and steady-state conditions are performed, e.g. on the influence of steam or of oxygen depletion conditions. Currently a new large test vessel REKO-4 is under construction for testing PAR behaviour under natural convection conditions. It will provide various possibilities for instrumentation to measure temperatures and gas compositions and in particular it will be equipped with particle image velocimetry (PIV) for measuring the flow field around the PAR.

2.1 Small Scale Test Facility REKO-3

Experimental studies on the operational behaviour of a recombiner section are performed at the REKO-3 test facility (Fig. 2.1). The experimental set-up allows the investigation of catalyst samples inside a vertical flow channel under well defined conditions comprising gas mixture, flow rate and inlet temperature. The catalyst sheets (stainless steel coated with washcoat/platinum catalyst material) are arranged in parallel forming vertical rectangular flow channels. Such a set-up represents a box-type recombiner section of AREVA design. The correlation of the hydrogen conversion and catalyst temperatures with the experimental parameters serve basically to clarify the interactions of reaction kinetics, heat and mass transfer, and the flow conditions inside the recombiner. Inside of the configuration the distribution of the catalyst temperatures and the gas composition in vertical flow direction are measured (Fig. 2.2).



(a) (b)

Figure 2.1: REKO-3 test facility: (a) partially isolated, (b) schematic view

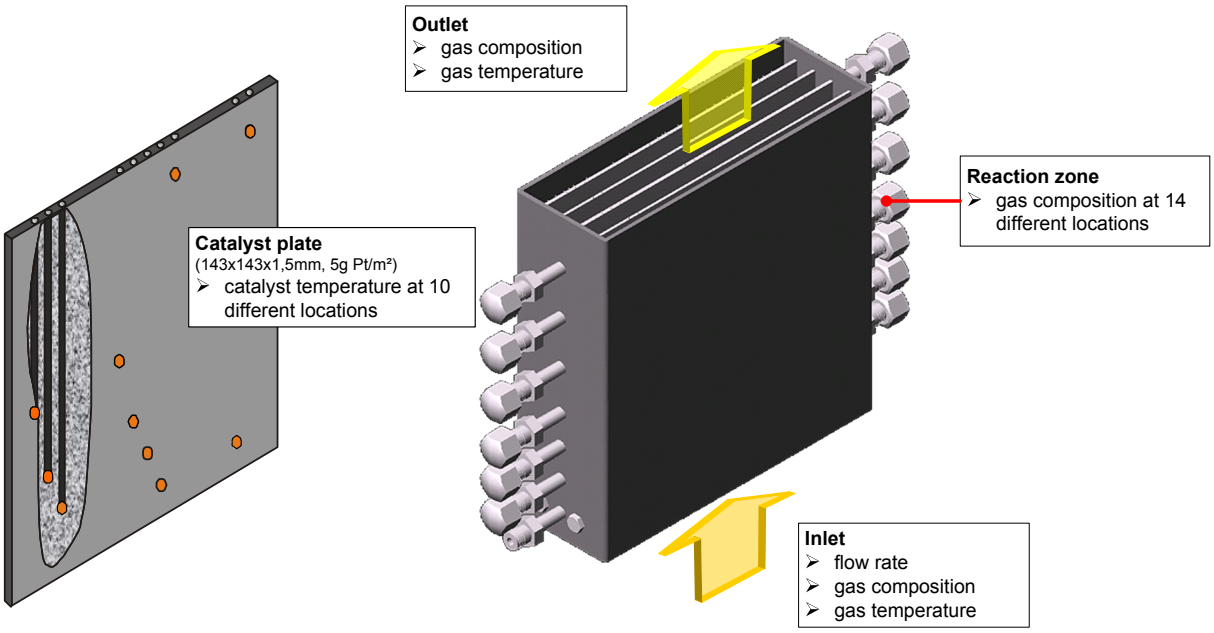


Figure 2.2: REKO-3 measuring points

For measuring the distribution of the catalyst temperature the catalyst sheets are equipped with thermocouples. In order not to disturb neither the gas flow nor the catalyst coating, drillings were manufactured inside the rear edge of the plates by means of spark erosion (0.6 mm) enabling thin thermocouples (0.5 mm) to be inserted at different locations inside the samples. For the measurement of the gas concentrations in the flow channel along the catalyst sheets, a probe head is introduced at different vertical positions allowing measurement of the hydrogen and oxygen depletion in flow direction. A total of 14 sample points has been implemented. The measurement gas is conducted from the sample point through a cooler and condensate trap. Hydrogen and oxygen concentrations are measured in line by separate systems (Fig. 2.3).

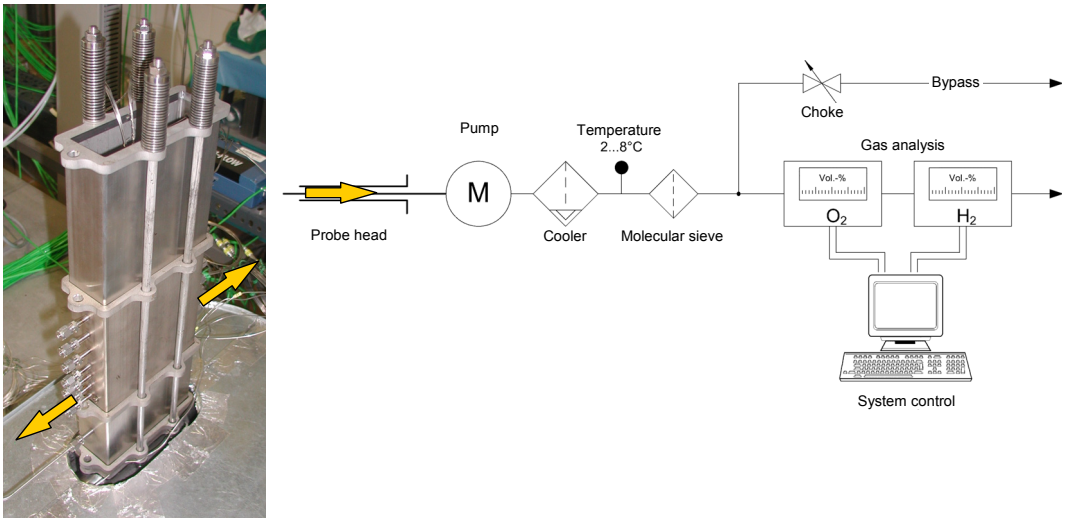


Figure 2.3: Flow sheet of the REKO-3 gas analysis section

The uncertainty of the different measurement components lies within 1 % of the measurement range. However, while the temperature measurement provides very robust data due to optimal contact with the catalyst and avoided flow interaction, the gas concentration measurements are subject to several disturbances. On the one hand, the measurement location can't be determined exactly as the probe gas is sampled from an undefined volume. On the other hand, changing of the background gas composition along the catalyst sheets causes deviations due to the measurement principle (heat conductivity sensor). A quantification of these combined measurement errors is not possible.

Some exemplary measurement results are given in Fig. 2.4. These steady-state distributions of the hydrogen concentration (left side) and the catalyst temperature (right side) were obtained at 2 vol.% and 4 vol.% inlet hydrogen concentration, the inlet gas temperature of 25°C and a flow rate of 0.8 m/s. The symbols represent measuring values while the lines are added for the sake of clarity. The measured values are plotted on the horizontal axis in order to illustrate the vertical arrangement of the catalyst plates.

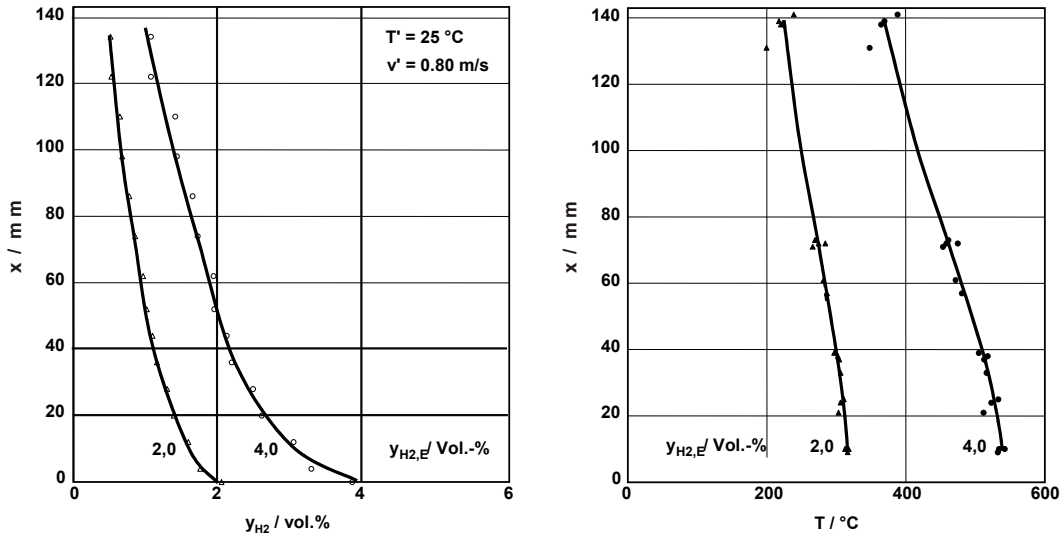


Figure 2.4: Steady-state hydrogen depletion (left side) and catalyst temperatures (right side) along the catalyst sheets for two different hydrogen inlet concentrations at 25°C inlet temperature and a flow rate of 0.8 m/s

The main part of the conversion reaction takes place in the very first area of the catalyst surface. This is reflected by the first sharp concentration drop as well as by the temperature profile where the maximum temperature is located close to the leading edge of the catalyst sheet (x = 0 mm). The temperature rise closer to the trailing edge is to some extent caused by heat conduction and convective

heat transport. Maximum temperatures reach the conventional ignition limit of about 560°C already at a hydrogen concentration of 4 vol.% hence representing the risk of an unintended ignition.

The experimental results obtained have been described in detail by Drinovac (2006). In general, the experiments have been performed for three different flow rates (0.25 m/s, 0.5 m/s, and 0.8 m/s), for three different inlet gas temperatures (25°C, 70°C, and 110°C), and for hydrogen concentrations between 0.5 vol.% and 5.0 vol.%. Specific attention has been paid to the effect of steam and oxygen starvation on the conversion rate. On-going experiments deal with the ignition of the gas mixture on hot catalyst sheets (table 2.1).

Issue	Experimental data available	Validation performed
Standard reaction kinetics	✓	✓
Influence of steam	✓	✓
Lack of oxygen	✓	✓
Ignition criteria	on-going	

Table 2.1: Experimental results and model validation matrix

In addition to these experiments representing the reference case using catalyst sheets fully coated on both sides, specific catalyst arrangements have been investigated including:

- sheets only partially coated (the first 27 mm at the leading edge were left uncoated),
- sheets coated with stripes of catalyst material,
- sheets coated on both sides with alternating stripes of catalyst material, and
- additional uncoated sheets arranged between the catalyst sheets.

2.2 REKO-4 Test Vessel

In order to study the operational behaviour of PAR under natural flow conditions and to study the chimney effect on the PAR operation in detail a new facility (REKO-4) is presently constructed at Jülich. The pressure vessel with an inner diameter of 1.4 m and a height of 4 m is designed for a pressure of 25 bar.

A total of 25 flanges will allow the accessibility of the vessel with different measurement techniques. Foreseen measurements inside the vessel are basically pressure, gas temperature and hydrogen/oxygen concentration. The PAR device will be equipped with thermocouples for catalyst and gas temperature measurement and hydrogen/oxygen sensors. Most challenging measurement will be the use of particle image velocimetry (PIV) for the measurement of the flow field at the inlet and the outlet of the PAR. On the one hand, these information are essential in order to determine the PAR throughput and efficiency. On the other hand, this high-resolution measurement technique provides data suited for CFD validation. In general experiments will study aspects of the operational behaviour of small PAR devices when the flow rate is solely induced by the heated catalyst sheets. For this purpose, a defined amount of hydrogen will be released into the air-filled vessel.

After start-up of the exothermal catalytic reaction the buoyancy effect is expected to fuel the PAR device. The hydrogen conversion will be monitored by sensors inside the vessel. Due to the option of positioning the PIV device in different locations it is expected to visualise the flow pattern in different relevant areas around the PAR. First experimental results are expected for late 2008.

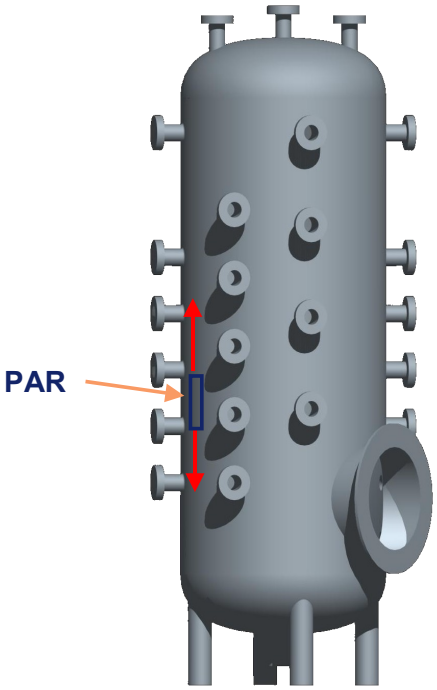


Figure 2.5: REKO-4 vessel

3 MODELLING APPROACHES

There are several effects and phenomena related to PAR which need to be resolved in a higher detail than presently possible with lumped parameter (LP) codes and black-box models. These include local containment studies concerning the interaction of different safety measures as well as the detailed investigation of the thermo hydraulic phenomena inside a PAR. For these purposes different approaches have be developed at Jülich in order to model the catalytic surface reaction as well as the entire device. The simplest approach is the direct implementation of the manufacturer's empirical parameter correlations for calculating the hydrogen consumption rate. A more detailed approach is the implementation of REKO-Direkt, a mechanistic model to describe an entire PAR via USER-Fortran routines. For a detailed understanding and optimisation of the thermo hydraulic and transport phenomena CFD is used to model the reaction and all relevant transport phenomena at a single catalyst element.

3.1 Model Discussion

3.1.1 Detailed model

Heterogeneous catalysis on a coated surface can be described by several elementary steps as shown in figure 3.1 (left): The transport to the surface by convective and diffusive transport in the bulk flow and film diffusion trough the boundary layer. In a porous catalyst, the reaction occurs inside the pores: therefore the reactants must diffuse into the catalyst where they encounter active sites and the reaction takes place. The intrinsic rate depends on the gas phase concentration at the active sites; the pore diffusion can be described by different modes which depend on the pore size. Detailed schemes which describe the surface reaction are known, for example by Warnartz et al. (1994).

The REKO-3 test series and previous work performed at Jülich (Reinecke et al., 2004) revealed that in the present case the rate determining step of the catalytic recombination of hydrogen and oxygen is the transport of the products and educts from and to the surface. The implemented CFD model is based on this elementary understanding. For the simulation of the catalytic process only the transport of the

species is considered (figure 3.1 right). The outer surface of the catalytic coating is modelled as a wall. The chemical reaction is implemented as a single step reaction

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O + \Delta h_r^o \tag{1}$$

by means of sinks and sources of mass, enthalpy and momentum in the cells adjacent to the wall.

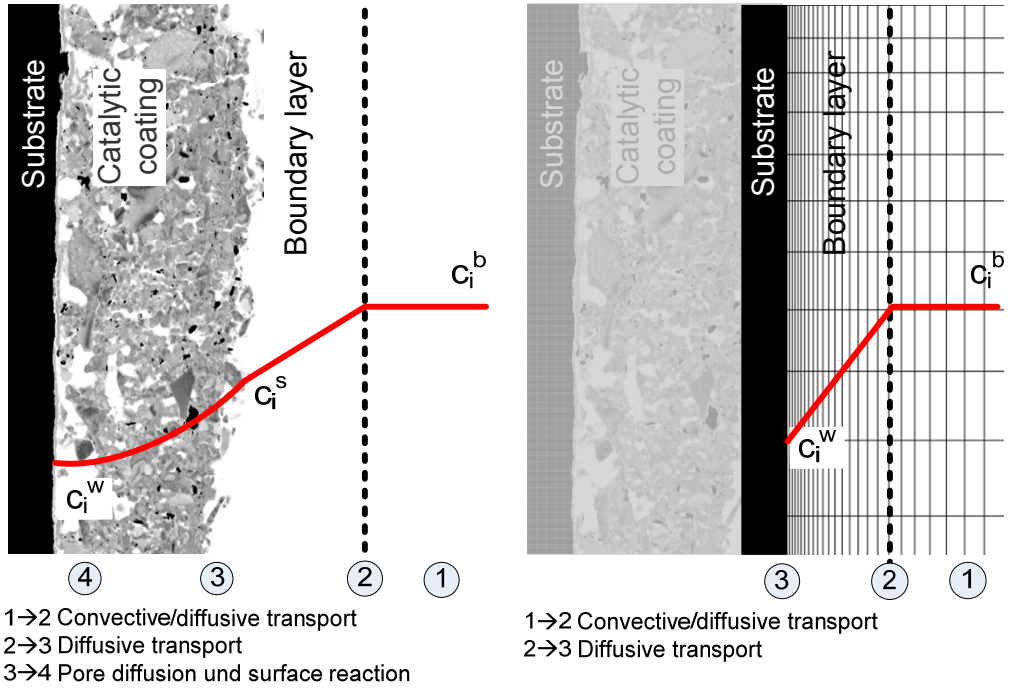


Figure 3.1: Heterogeneous catalysis: Theory and model

The prediction of the reaction rate is done by fully resolving the species boundary layer, which allows solving the reactants flux by Fickian diffusion only. Consequently the reaction rate can be described as

$$\dot{r}_i'' = \bar{c} \cdot \left(D_i + \frac{\upsilon_t}{Sc_t} \right) \frac{\partial X_i}{\partial y}\bigg|_w \qquad i: H_2, O_2 \tag{2}$$

where c is the molar concentration of the mixture, D_i is the effective diffusion coefficient of the species i in the mixture, ν_t/Sc_t is the turbulent diffusion coefficient and X_i the molar fraction of the species i. To enable the model to predict the reaction rates under oxygen starvation conditions as well the transport of oxygen is also considered. The system of compressible Navier Stokes equations is closed by the k-ω based shear stress transport (SST) turbulence model in order to use this low Reynolds approach and integrate up to the wall and avoid the use of wall functions. The *i*-species are described by the ideal gas equation of state. As buoyancy is the major driving force, the full buoyancy model including the production and dissipation of turbulence is included. The radiative heat transfer between the plates and also with the environment is considered by a Monte Carlo model.

This modelling approach has been developed under application of the ERCOFTAC best practise guidelines (Casey and Wintergerste, 2000) and validated against the REKO-3 test series for plate type catalyst sheets (AREVA design). Figure 3.2 shows exemplarily the temperature profiles in the catalyst sheets and the hydrogen concentration decay in the flow channel for different hydrogen inlet concentrations and a typical flow velocity of 0.8 m/s in a PAR.

The catalyst temperature profiles are predicted quite well by the model, except a slight over prediction at the end of the catalyst sheet in some cases due to some uncertainties with regard to the radiative heat exchange with the REKO-3 channel and outlet. Comparing the concentration profiles with the experimental data is difficult as this measurement allows no point or profile measurement, so for validation purpose two extreme cases are considered: The values at the symmetry plane between the plates (solid line) as a quasi point measurement and an massflow average over the channel cross

section (dashed line). The numerical model predicts the concentration profiles, and with it the entire reaction rate quite well in a reasonable agreement to the experimental results.

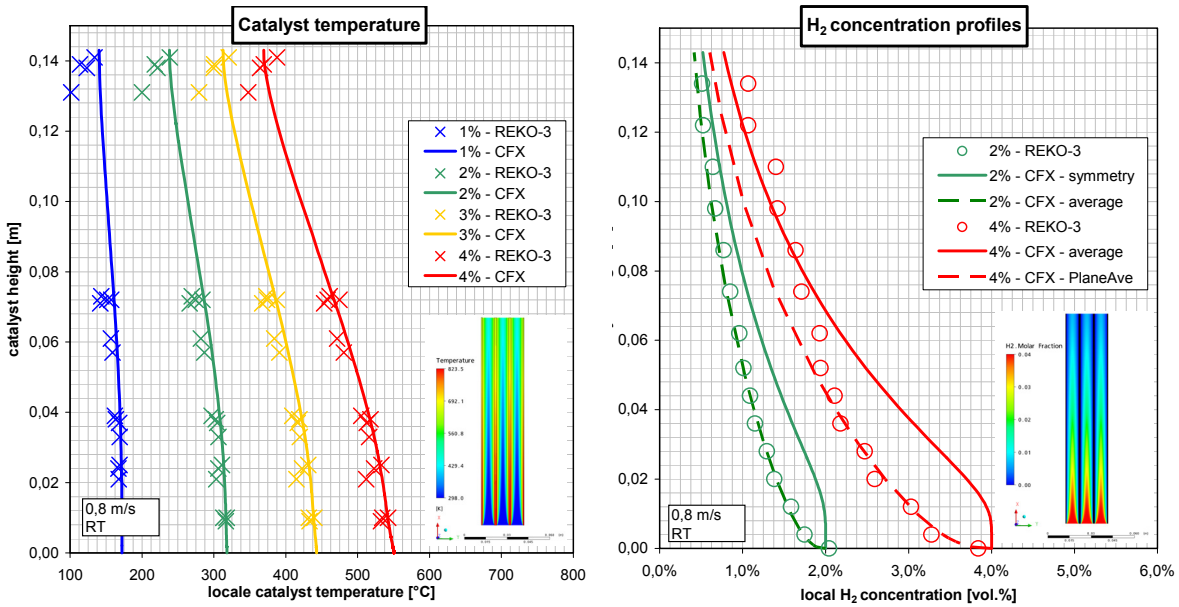


Figure 3.2: Temperature und concentration profiles: Experimental and CFD modelling results

This modelling approach has its advantage in predicting the detailed thermo hydraulic and transport phenomena in a PAR channel and is used for the assessment of new catalyst designs. For the study of an entire PAR operational behaviour it is to cost intensive to model all catalyst elements this degree of detail.

3.1.2 Entire PAR modelling approaches

Up to now for the PAR system design and accident analysis the only available and for designated cases validated models are the manufacturer's correlations which are implemented in integral LP containment codes. These empirical correlations are based on the large scale experiments performed to demonstrate PAR performance under realistic conditions (Bachellerie et al. 2003).

These models describe the hydrogen consumption rate for a reference PAR type as a function of the ambient gas concentrations and the pressure: The H_2 consumption rates proposed by the manufacturers are given by the following empirical correlations (Bachellerie et al. 2003):

AECL $$\dot{r}_{H2} = \left(0.15196 \cdot C_{H2} + 0.0126 \cdot C_{H2}^2\right) \cdot \left(\frac{198}{T}\right)^{1.10974} \cdot P^{0.57769} \quad \left[\frac{kg}{h}\right] \tag{3}$$

AREVA $$\dot{r}_{H2} = \eta \cdot \min\left(X_{H2}, 2 \cdot X_{O2}, 0.08\right) \cdot \left(A \cdot p + B\right) \cdot \tanh\left(X_{H2} - 0.5\right) \quad \left[\frac{g}{s}\right] \tag{4}$$

NIS $$\dot{r}_{H2} = 1.134 \cdot C_{H2}^{1.307} \cdot \left(\frac{P}{RT}\right) \quad \left[\frac{g}{s}\right] \tag{5}$$

where X_i is the volume fraction and C_i the volumetric concentration [m³/m³] of the hydrogen and oxygen respectively, p is the pressure (bar), T the absolute temperature (K) and A and B and the other constants respectively are model parameters which include all residual influences and conditions at the validation experiments and depend on the recombiner model. In the AREVA approach η can be used to describe the PAR efficiency under different conditions (eg. oxygen depletion or spray).

As a first approach these correlations can be scaled and implemented by means of volumetric sinks and sources of energy, mass and momentum or as a black-box directly in CFD as described for example by Kudriakov et al (2008). Similar approaches applied in the frame of the EU network SARNET (Severe Accident Research Network) PARIS (PAR Interaction Studies) studies (Dabbene et al., 2007) by different partners.

These empirical models are validated for the specific experimental conditions present in the original tests. However, for detailed CFD studies they do not provide relevant parameters, such as catalyst or box temperature to assess the ignition risk. For this reason, REKO-Direkt, a 2D detailed mechanistic black-box model based on Fortran 90 was developed at Jülich (Böhm, 2006). The principal structure of REKO-Direkt and its interface to CFX are shown in figure 3.3.

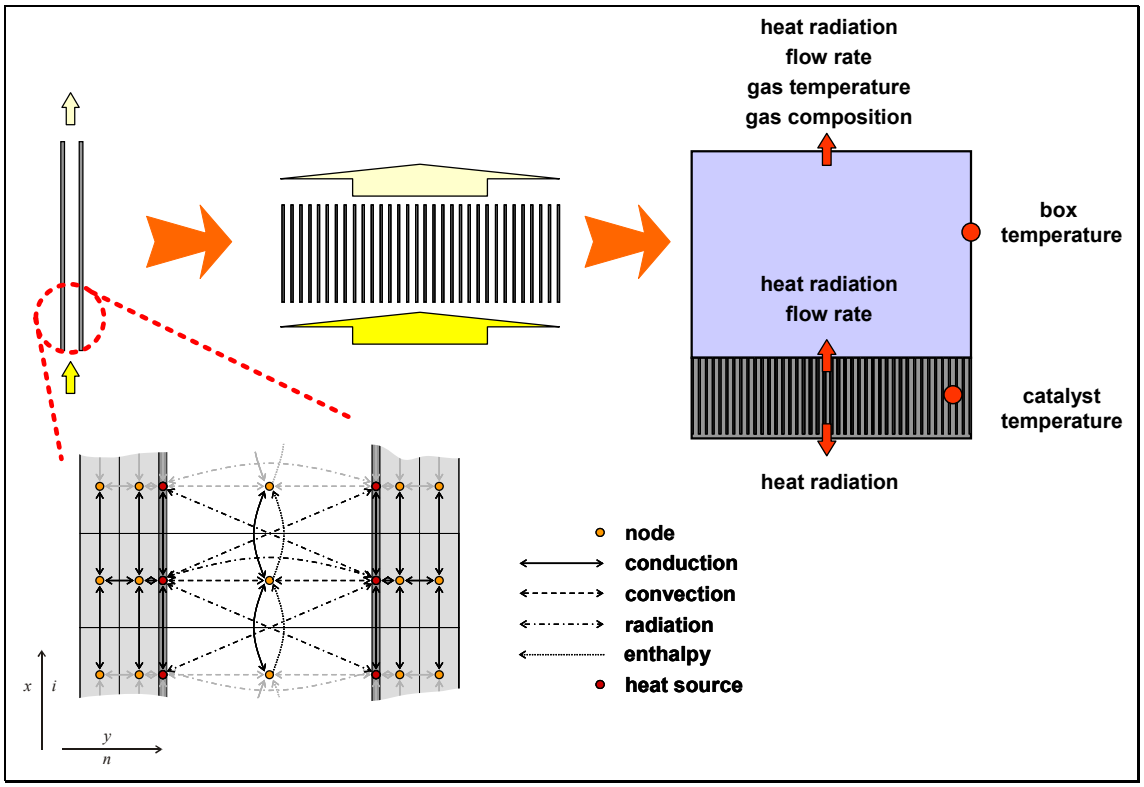


Figure 3.3: Structure of REKO-Direkt and interface to CFX

For a single channel local reaction rates are calculated by means of a mechanistic transport approach

$$\dot{r}_i'' = Sh \cdot \frac{D_i}{d} \cdot \Delta C_i \qquad i : H_2, O_2 \quad . \tag{6}$$

Here Sh is the local Sherwood number, D_i the effective diffusion coefficient of the species i in the mixture, d the hydraulic diameter and ΔC_i the molar concentration of the species i. The system of mass and energy balances is solved directly, which allows gaining a fast and robust solution. This single channel is extrapolated to a full recombiner catalyst section to calculate in a last step the buoyancy driven flow through the PAR box as well as the radiative and convective heat fluxes from the PAR to its environment. REKO-Direkt provides also the efficiency of the PAR and the maximum catalyst temperatures which can be used for further risk and safety assessment.

REKO-Direkt has been validated against the REKO-3 database. Figure 3.4 shows as an example the temperature profiles and hydrogen concentration decay for different H_2 inlet concentrations and flow velocities. The code reproduces the temperature distribution and reaction kinetics for the experimental test cases (table 2.1) quite well.

Natural convection trough the PAR box is already implemented and predicts credible values for the flow velocity, compared to the integral large scale experiments. As these experimental database of the integral experiments are mainly not accessible and detailed enough, this phenomenon will be investigated in more detail at the REKO-4 test vessel, and give a more quantitative validation data base.

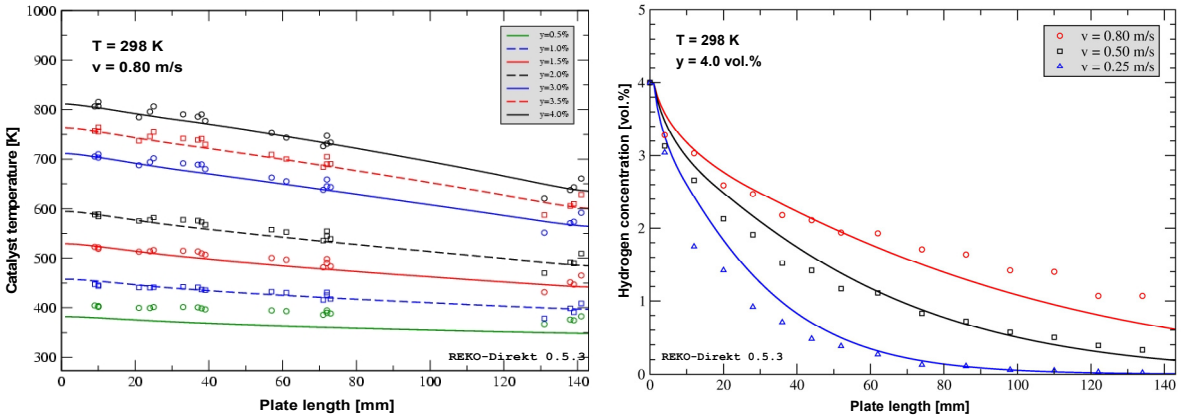


Figure 3.4: Temperature und concentration profiles: Experimental and REKO-Direkt results

The implementation of REKO-Direkt via USER-Fortran routines into CFX is currently in progress.

3.2 Application/Results

In the frame of SARNET WP12-2 containment atmosphere mixing, PAR interaction studies (PARIS) are performed in order to investigate in general adopted models and approaches and focus on the impact of PAR elevation on the phenomena of stratification (PARIS-1). In the frame of this study an AREVA FR90/1-150 like PAR was considered in a 2D rectangular domain. The hydrogen conversion was modelled by means of the empirical AREVA correlation (equation 4). In PARIS-1 a closed 5mx5m domain, fitted with two PARs was addressed (figure 3.5 left). In order to compare PAR and containment interactions heat and mass transfer to the walls was not considered. The starting point for the 3000 seconds calculation was a homogeneous mixture at 100°C, containing 5 vol.% H_2 in dry air and steam at saturation conditions. In the first 300 seconds the flow was nearly symmetric (figure 3.5 middle and resulted after about 400 seconds in a stable thermal stratification in the domain. As thermally driven convection loops have difficulties to mobilise the cold H_2 rich gas located near the floor below the PAR inlet (figure 3.5 right), this scenario develops into a diffusion controlled situation. The elevation of the PARs had an influence on the thickness of the bottom layer, but could not resolve it anyway.

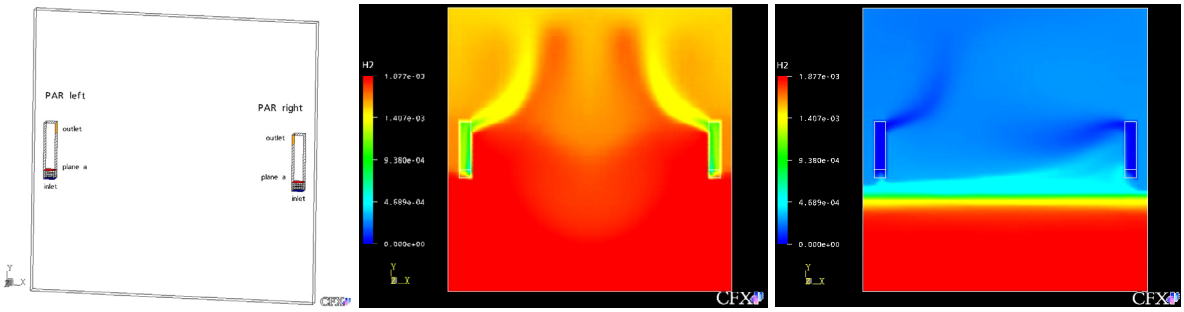


Figure 3.5: PARIS-1: Geometry, hydrogen mass fractions operation after 10s and diffusion controlled scenario after 400s

The main reason for the formation of the bottom layer was the artificial assumption of adiabatic walls. In a real situation heat transfer to the compartment walls and condensation would result in an enhanced mixing of the atmosphere. This was demonstrated in a further calculation with constant wall temperatures revealing that the bottom layer is dissolved after 500 seconds. Nearly adiabatic situations are however imaginable and the phenomenon of thermal stratification has occurred in some integral containment experiments. Consequently, the relevance of detailed studies has been affirmed by this benchmark exercise.

Currently, PARIS-2 is progress investigating the impact of forced downward flow conditions on the PAR operation.

4 SUMMARY AND FUTURE WORK

The numerical modelling of operational behaviour of PAR is an important task in SA research and analysis. In order to complement the existing integral database, Jülich performs separate effect tests at the small scale test facility REKO-3 under well defined conditions to investigate the reaction kinetics on the catalyst elements of a PAR. A new test vessel REKO-4 will be dedicated to the assessment of PAR behaviour under natural convection conditions.

Based on these experimental results a detailed model has been developed and implemented in CFX for describing the H_2 conversion process at a single catalyst element. This model is used at Jülich for the optimisation and design of innovative catalyst designs. In order to model an entire PAR currently the manufacturer's correlations are directly implemented in CFX. To overcome their limitations of these empirical parameter models REKO-Direkt, a mechanistic model will be implemented by means of USER Fortran routines. First common recombiner interaction studies within SARNET affirm the need of detailed investigation of PAR operational behaviour. This work will be continued in the SARNET and at Jülich.

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