STATE OF THE ART
ON HYDROGEN PASSIVE AUTOCATALYTIC RECOMBINER

(EUROPEAN UNION PARSOAR PROJECT)

F. ARNOULD (1), E. BACHELLERIE (1),
M. AUGLAIRE (2), B. DE BOECK (3), O. BRAILLARD (4),
B. ECKARDT (5), F. FERRONI (6), R. MOFFETT (7), G. VAN GOETHEM (8)

(1)   Technicatome, PO Box 34000, 13100 Aix-en-Provence, France
(2)   Tractebel Energy Engineering, 7 avenue Ariane, 1200 Brussels, Belgium
(3)   Association Vincotte Nuclear, 157 avenue du Roi, 1190 Brussels, Belgium
(4)   Commissariat à l'Energie Atomique, Centre de Cadarache, 13108 Saint-Paul Lez Durance, France
(5)   Siemens AG, PO Box 10 10 63, 63010 Offenbach am Main, Germany
(6)   Electrowatt Engineering Limited, PO Box 8037, 8037 Zurich, Switzerland
(7)   Atomic Energy Canada Limited, PO Box ROE ILO, Pinawa, Canada
(8)   European Commission, 200 rue de la Loi, 1049 Brussels, Belgium

KEY WORDS: SAFETY, HYDROGEN HAZARD, PASSIVE DEVICE, ACCIDENT, QUALIFICATION

ABSTRACT

This paper presents an overview of the European Union PARSOAR project, which consists in carrying out a state of the art on hydrogen passive autocatalytic recombiner (PAR) and a handbook guide for implementing these devices in nuclear power plants. This work is performed in the area « Operational Safety of Existing Installations » of the key action « Nuclear Fission » of the fifth Euratom Framework Programme (1998-2002).

Although lots of publications about recombiners have been published for the last ten years, no synthesis has been performing yet. The aim of the PARSOAR project is to make up this lack and to answer needs of all the nuclear technology partners. The project partners are representative of industry, safety organisations, and research institutes, coming from several countries (Belgium, Canada, France, Germany, and Switzerland).

The first part of the work (the state of the art on catalytic recombiners) is already performed. It tackles the following items: (1) presentation of the recombination reaction (thermo-chemical principle), (2) presentation of the commercial models, (3) comparison with other hydrogen mitigation systems, (4) presentation of the main experimental activities, (5) presentation of catalytic recombiner qualification, (6) hydrogen ignition risk induced by catalytic recombiner, (7) use of numerical codes to assess recombination rate and to simulate recombiner behaviour, and (8) presentation of national approach about PARs implementation in NPPs.

The present study shows that the catalytic recombiner is the most adequate system to mitigate the hydrogen hazard in a nuclear power plant because of its efficiency both in design-basis accident and in beyond-design-basis accident, its passive characteristic, its well known technology (chemical and physical processes), its well defined maintenance, and its low cost compared with other hydrogen mitigation systems.

It can be considered that designers have achieved their development: they have been successfully tested their devices in design-basis accident and severe accident conditions in their own facilities or in independent facilities. Few complementary experimental tests about poisoning effect or for simulating design-basis accident conditions in an inerted boiling water reactor, should be performed to complete the qualification.

Numerical models on the catalytic recombiner behaviour have been developed, and their integration in global computer codes are in progress. However, these models are insufficient because they can not simulate the probable hydrogen ignition phenomena inside the catalytic recombiner (hot catalyst plates), the degradation or destruction of the device, and the propagation of the combustion wave outside the recombiner.

To conclude, a first inventory of the national practices for implementing catalytic recombiners in nuclear power plants makes it possible to outline a common approach from the hydrogen sources quantification to the catalytic recombiner management. The development of this common approach will be the subject of the second part of the project with the writing of a handbook guide.

33 / 21

INTRODUCTION

The Three Mile Island (TMI-2, 1979) accident focused the attention of the nuclear safety community on the threat to containment posed by the large hydrogen amounts released into the containment building during and after a severe accident. It is believed that rapid oxidation of the zircaloy cladding by the steam generated from 150 to 600 kg of hydrogen [1]. Much of this was burned inside the containment building, causing a transient pressure rise of roughly 200 kPa whereas the containment design pressure was about 500 kPa.

Several research programs to study hydrogen behaviour and control during hypothetical accidents were also initiated at the beginning of the eighties. The two main mitigation options were the containment atmosphere dilution with an inert gas to prevent combustion, and the deliberate hydrogen ignition at low concentrations to limit the consequences of combustion phenomena.

In the nineties, a new mitigation strategy based on the catalytic oxidation of hydrogen using oxygen from the containment atmosphere and a noble metal as catalyst emerged: the passive autocatalytic recombiner (PAR). This mean to control hydrogen hazard in nuclear power plants is very successful because of: (1) its passive characteristic, (2) its large domain of good efficiency (design-basis accident and beyond-design-basis accident), (3) its robustness towards accidental conditions and internal hazards, (4) a reduced cost compared with other mitigation strategies, and (5) a well-defined maintenance.

PRINCIPLES OF PASSIVE AUTOCATALYTIC RECOMBINER

The chemical reaction between hydrogen and oxygen to form water $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$, is an exothermic radical reaction ($\Delta H^0_r = -238$ kJ/mol) and starts only after overcoming the required activation energy. This reaction in air starts autonomously only at temperatures of about 600-650 °C.

The activation energy for the recombination of hydrogen and oxygen can be significantly reduced by the use of catalytic substances, so that the reaction can start at low temperatures automatically without propagation of the reaction to the surrounding atmosphere. The mechanism of a catalyst (platinum, palladium) is to decrease the bounding of the hydrogen molecules and to form radicals that will react more easily with the oxygen radicals. Catalytic recombiners favour the reaction $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ by lowering the activation energy threshold so that the chemical reaction takes place at low temperature and concentration (figure 1).

The catalytic oxidation of hydrogen on metals follows the Langmuir-Hinchelwood mechanism. The two main steps are: (1) the diffusion of the reactants on the catalyst, and (2) the reaction of absorbed reactants on the catalyst.
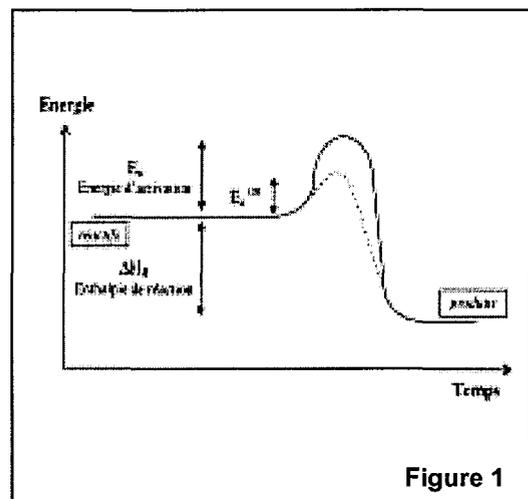

Figure 1

A catalytic recombiner is described as « passive » because such a device is self-starting and self-feeding, and requires no external energy. A passive autocatalytic recombiner comes into action spontaneously as soon as the hydrogen concentrations begins to increase in the reactor building atmosphere [2]. In practice, catalytic recombiner starts up with hydrogen concentration equal to 1-2 %.

A passive autocatalytic recombiner consists of a vertical channel (stack) equipped with a catalyst bed in the lower part. In case of accident, the catalyst bed is in contact with the gas mixture of the containment. Hydrogen molecules coming into contact with catalyst surface are reacted with oxygen in air. The heat of the reaction at the catalyst surface induces convective flow, without mechanical assistance or outside power.

The heat release of the reaction in the lower part of the recombiner causes a buoyancy accelerating the inflow rate and thereby feeding the catalyst with a large amount of hydrogen bearing gases ensuring high efficiency of recombination (figure 2). A natural air circulation starts linked to the passive autocatalytic recombiner in the partly confined control volume around it. The natural convective flow currents promote mixing of combustible gases in the containment, and avoid probable hydrogen over-concentrations (« hydrogen pockets »). The natural air circulation assures a continuous air supply to the catalytic recombiner.
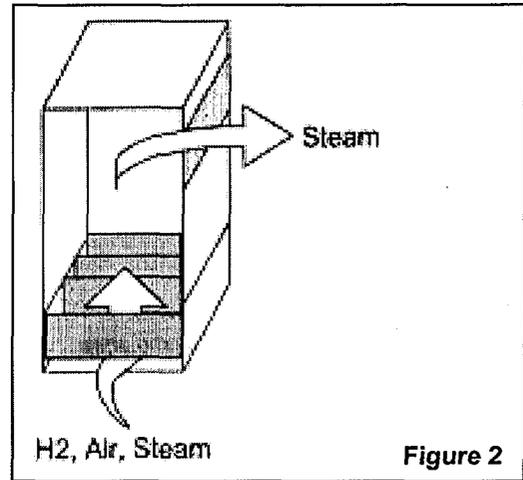

Figure 2

## PRESENTATION OF THE COMMERCIAL MODELS

Different types (catalyst) and models (dimensions, chimney) of passive autocatalytic recombiners have been developed. The four designers are Atomic Energy Canada Ltd. (AECL), Electrowatt Engineering Ltd. (EWE), Nis company, and Siemens KWU. For each designer, a description in four points is given: (1) a history of the development, (2) a presentation of the design, (3) a presentation of the catalyst used, and (4) an overview of the qualification tests.

Atomic Energy Canada Limited

The AECL catalyst and recombiner design is the result of more than 15 years of research. The catalyst were developed, originally, for the purpose of heavy water manufacturing by way of a catalytic exchange process. Application of these catalyst materials in recombiners for containment applications began in the late 1980's. The first application was a passive recombiner, qualified for use in control of radiolytic hydrogen in the head-space of a pool-type experimental reactor of AECL design in 1988 [3].

The AECL recombiner is designed for compactness and ease of engineering into containment. The design consists of an open-ended rectangular box (32 cm × 62 cm × 52 cm) with an attached cover and gratings (figure 3). The cover and gratings provide physical protection to the internal elements from sprays. Inside the box, flat rectangular catalyst elements are arranged parallel to the direction of gas flow. These elements are spaced 2 cm apart to promote optimal natural convection flow. They can be accessed by removing or pivoting the cover.

The AECL catalyst operates at temperatures up to 1000 K without loss of wet-proofing or catalytic activity and is unaffected by high radiation exposures. The recombiner is self-starting at low hydrogen concentrations in steam-saturated atmospheres at temperature as low as 13°C.

Figure 3

3
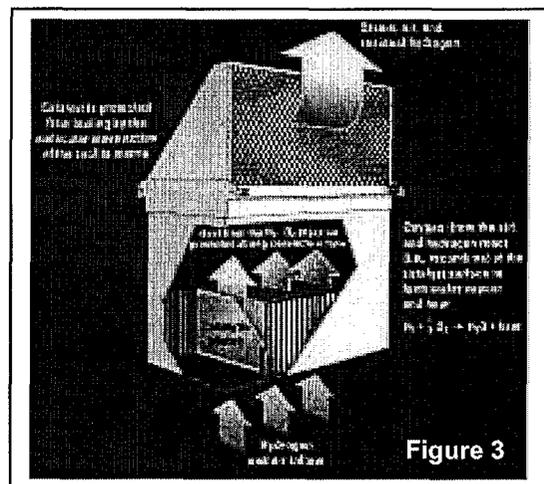
The AECL recombiner has been qualified through extensive testing. Function and performance of the recombiner have been demonstrated in the 6.6 m³ and 10.7 m³ Containment Test Facility (CTF) vessels at AECL Whiteshell Laboratories using a full-scale prototype and a 1/10-scale test model. Environmental qualification testing was conducted in the 120 m³ Large Scale Vented Combustion Test Facility (LSVCTF) at Whiteshell Laboratories and in the French H2PAR facility. Performance tests confirm recombiner self-start behaviour in cold, wet conditions and demonstrate recombiner capacity in typical post-LOCA environmental conditions. Once started, the removal capacity normalised to the inlet-section area of the recombiner scales approximately linearly with the hydrogen concentration.

Electrowatt Engineering Limited

The commercial passive autocatalytic recombiner developed by Electrowatt Engineering AG and CCI AG (formerly Sulzer Thermtec) is called KATAREK. The original concept has been developed by Gesellschaft für Anlagen und Reaktorsicherheit GmbH (GRS) and Forschungszentrum Jülich GmbH (KFA) in Germany since 1982 which is based on the full metallic catalysis principle [4].

The KATAREK device or module consists of a housing in the form of a hollow square or rectangular section. The standard dimensions are 300 x 300 mm. The total height as well as the cross-sectional surface of the module can be adapted to actual conditions. Versions with a total height of 1200 mm and 1900 mm have been tested at full scale. The catalyst plates are placed at the bottom part of the housing in layers. The full-metallic catalyst plates of each layer are slightly inclined and fixed together with holding plates. The various layers are perpendicular to each other. This type of layout guarantees an optimum mass transfer between the gas and the catalyst. Through the perpendicular and inclined arrangement it is possible to obtain a mixing effect, so that the gas mixture flow is divided united again, keeping the boundary layer very thin. This ensures an easy transport of the reactants to the catalyst surface and is an important prerequisite for a good recombination rate (figure 4).

In the full metallic catalyst adequate porosity is obtained without an intermediate ceramic coating by means of the direct coating of a catalyst powder with 95 % palladium, 4 % of nickel and 1% of copper by a high temperature injection. Palladium has a higher activity than platinum for the recombination of hydrogen and oxygen. The high temperatures injection is performed by thermal spraying with an electrical gas discharge (plasma spraying). The thermal spraying gives rise to a strong bond between the support material and the coating due to the formation of a diffusion layer at the interface.
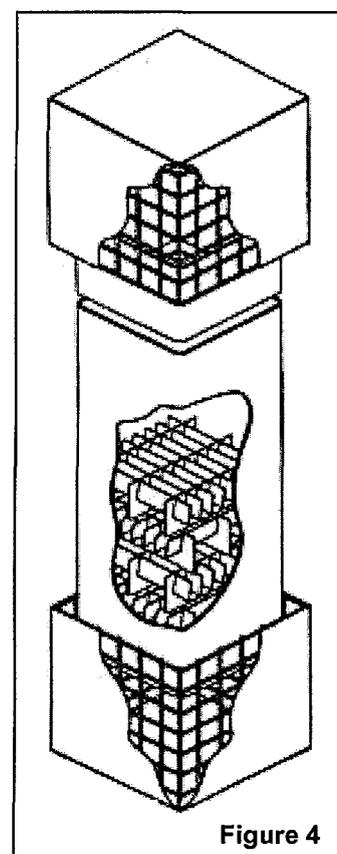

Figure 4

Integral qualification tests have been performed with a full size section (15 × 15 cm) of a KATAREK module with high thermal inertia at the KALI H2 facility to measure the depletion rate. Typical containment atmospheres for different accident scenarios have been simulated.

NIS Company

The catalytic recombiner developed and commercialised by NIS Company was sponsored by the German utility RWE and qualified in cooperation with Degussa as catalyst supplier, the Battelle Institute to perform experimental tests, and the Technical University of Munich to analyse the performance characteristics.

NIS catalytic recombiner units are supplied in a variety of sizes to assure the required depletion rate. Half meter long chimney prolongation section is available to increase the rate of depletion. The outer dimensions of the inlet of the catalytic recombiner composed by 88 cartridges (45 × 20 × 1 cm), are 1000 × 1000 mm (figure 5). The NIS catalytic recombiner contains flat rectangular cartridges filled with porous spherical ceramic pellets, which are coated with palladium. Such a device contains a total of 30 kg of hydrophobic spherical catalyst pellets, with 1-cm-wide open flow channels between the cartridges. The total weight of a full-size passive autocatalytic recombiner is about 170 kg. Between the cartridges, the device has open flow channels to allow heavier particles or aerosols in the atmosphere to flow through with little plugging of the pellet surface [5].
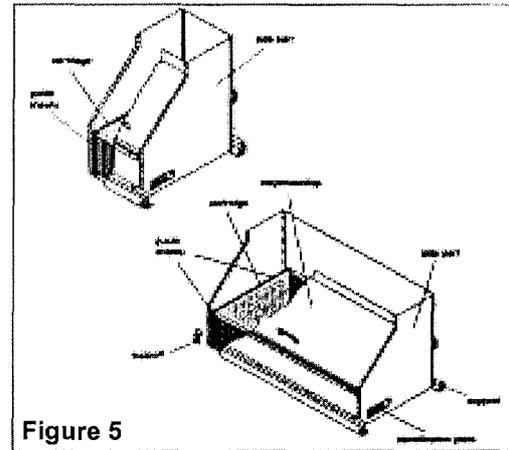

Figure 5

Spherical aluminium pellets with diameters between 4 and 6 mm are coated with the basic catalytic material, palladium (active Pd-impregnated shell 0.5 mm thick), and with a hydrophobic material on top of that. The hydrophobic coating is placed on each pellet to minimise start-up delays due to water on the catalyst surface (steam condensation or containment sprays). The pellets are enclosed in slotted steel sheet cartridges.

The performance of NIS catalytic recombiner was first characterized in the Battelle facilities. 41 preliminary experimental tests on recombiner models with full-height catalyst cartridges and a 11 × 11 cm cross-sectional flow area have been made. An additional 8 Sandia tests in a large multicompartment concrete containment model confirmed the performance of a full-size prototype and demonstrated the ability of the PAR to withstand burns of up to 10 % vol. hydrogen without structural damage.

Siemens KWU

The FR90/1 catalytic recombiner comprises a metal housing designed to promote natural flow, with the gas inlet arranged at the bottom and gas outlet at the top. Numerous parallel plates with a catalytically active coating are arranged vertically in the bottom of the housing. The cover of the housing at the top of the recombiner protects the catalyst against direct spraying of water and aerosol deposition, thus allowing recombiner operation under spray conditions (figure 6). Easy access of the catalytic plates is provided by way of a removable inspection drawer [6].
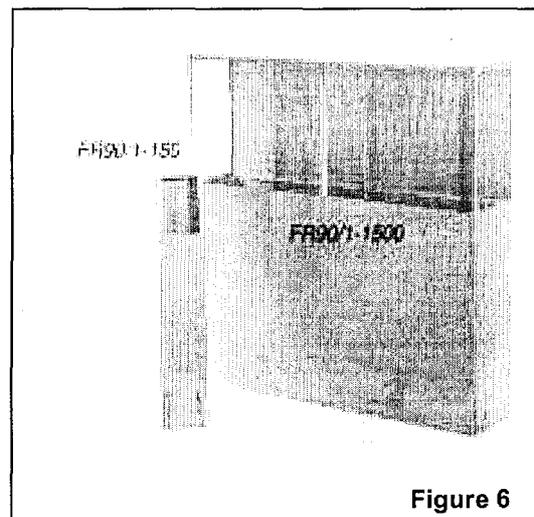
The catalyst consists of a thin stainless steel plate coated with a special multi-precious-metal catalyst. The catalyst allows low starting temperatures. Hydrophobic behaviour of the catalyst is ensured without additional layers. The units are therefore extremely temperature and radiation-resistant.

Figure 6

In addition to development tests on model and full-size Siemens catalytic recombiners, an extensive test qualification program was conducted to measure depletion rates under a range of hydrogen concentrations, steam/pressure conditions and various potential adverse poisoning conditions. Some tests were conducted in the Battelle multi-compartment facility. Independent organizations have participated in and/or performed qualification testing of the Siemens design, such as TÜV, CEA (spray impact, qualification in DBA and BDBA conditions), IPSN (qualification of the recombiner in presence of aerosols, ignition tests), EPRI and EdF, etc.

COMPARISON WITH OTHER HYDROGEN MITIGATION SYSTEMS

Other hydrogen hazard mitigation systems have been studied, developed and implemented in nuclear power plants. It is therefore interesting to review these systems to assess their limits and to compare their efficiency with the passive autocatalytic recombiners. The other mitigation systems implemented in nuclear power plants are: thermal recombiners, ignitors, inerting systems, and mixing systems. Another innovative concepts are nowadays in progress and are based on: hydrogen recombination, hydrogen permeatation, metal oxides reduction by hydrogen, and controlled combustion of organic matters (oxygen removal).

Thermal Recombiners

The thermal recombiners consist of a thermally insulated vertical metal duct with electric resistance metal sheathed heaters provided to heat a continuous flow of containment air (containing hydrogen) up to a temperature which is sufficient to cause a chemical reaction between hydrogen and oxygen. The recombiners are provided with an outer enclosure to keep out containment spray water (figure 7).

These recombiners consist of an inlet preheater section, a heater-recombination section, and a discharge mixing chamber that lowers the exit temperature of the air [7]. Air is drawn into the recombiner by natural convection and passes first through the preheater section. After that, the warmed air passes through and orifice plate and then enters the electric heater section where it is heated to 600-700 °C causing recombination. The main drawbacks of this system are the low recombination rate, the active characteristic, and the high cost of the maintenance.
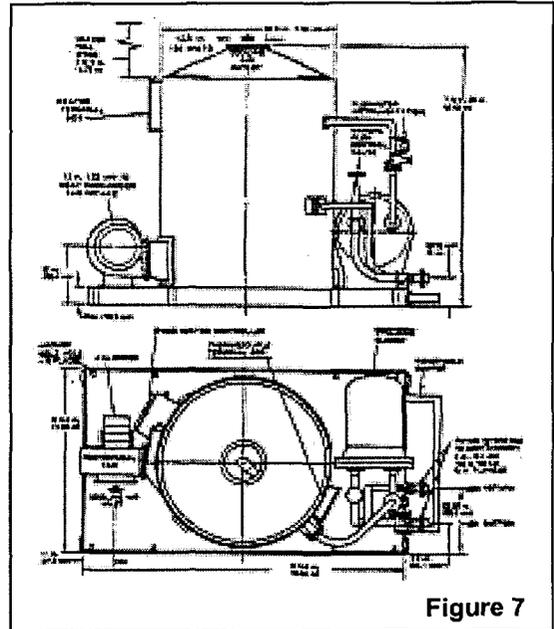
Figure 7

Ignitors

The principle of ignitors consists in creating deliberate ignition of combustion before reaching critical hydrogen-steam-air mixtures (high concentrations of hydrogen and oxygen, which would result in fast deflagration or detonation). The hydrogen burning concentration is about 4-6 % depending on the steam concentration. A combustion near the flammability limit leads to quite low pressure and temperature increases.

Several drawbacks have been identified for this system: (1) in case of fast hydrogen release in the containment, hydrogen concentration increases so quickly that the igniters may induce a local detonation, (2) ignition is not possible in steam inerted atmospheres (concentration above 50 %), and (3) deliberate ignition can occur in specific rooms with unknown hydrogen concentration.
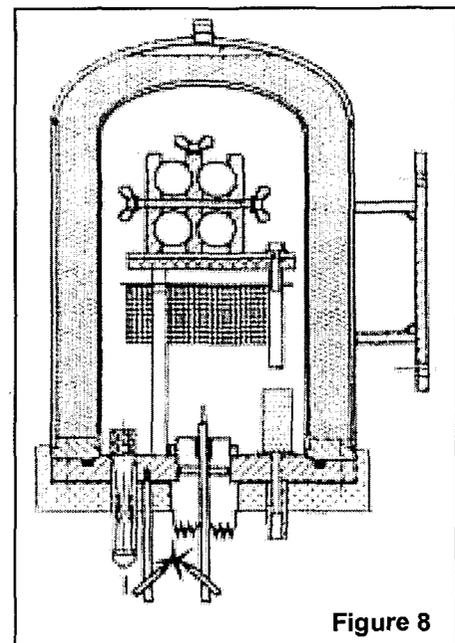
Figure 8

Inerting

Inerting systems consist in reducing the oxygen concentration below 5 % vol. by injection of inert element (nitrogen or carbon dioxide) in the containment. Inerting schemes control hydrogen combustion by limiting the supply of oxygen. They are suited for design-basis accidents (slow hydrogen concentration increase) and beyond-design-basis accidents (large and fast hydrogen releases).

Two systems are considered: (1) pre-inerting system that consists in maintaining an oxygen concentration below 5 % vol. in the containment for all situations (normal operation and accidental sequences), and (2) post-accidental inerting system that consists in injecting non-combustible (diluent) or combustion-inhibiting element (iron pentacarbonyl, halometallic compounds) into containment atmosphere following an accident but before release of significant quantities of hydrogen. The main drawbacks of these systems are the active characteristic, the technical complexity, and the important constraints under normal operation (pre-inerting) or under accidental sequence (post-inerting: short delay for decision).

Mixing Systems

A mixing system consists in diluting and homogenising the containment atmosphere with active components-systems (fans, spray system, helium injection) or passive systems (ice condenser). The intent of mitigation by mixing is to dilute the hydrogen such that the lower flammability limit (LFL) is not exceeded. Mixing can prevent the occurrence of flammable mixtures in localised regions of reactor building atmosphere or in compartments, as long as the ratio of the released hydrogen volume to total containment volume is small. These conditions are typical of accidents with moderate hydrogen source terms (DBA) in large containments.

Mixing systems may lead to turbulence phenomena in the reactor building, may aggravate the environmental conditions (possible de-inerting of the atmosphere by reducing steam concentration), and may initiate static ignitions (failure of fan inducing a spark ignition).

Hydrogen Recombination

Several possibilities of removing hydrogen from containments of pressurised and boiling water reactors, by innovative methods, are explored by the Forschungszentrum Jülich GmbH [8]. Development of innovative devices for hydrogen removal should mainly be based on passive, self-acting and self-operating principles. These may include utilisation of the boundary conditions and relevant driving forces like over-pressures, condensation energy, reaction heats, and temperature differences, assumed in accident scenarios as well as energy storage or removal potentials for improved system and component designs.

As with all technical systems, catalytic recombiners still possess a significant innovation potential. The main probable axes of development are: (1) the increase of conversion rates, (2) the improvement of the start-up behaviour, (3) the dissipation of the reaction heat, (4) a protection against aerosols at the recombiner inlet for the reduction of catalyst poisons, and (5) the use of already available surfaces for hydrogen recombination.

Some of the above items are the subject of approved and applied patents. They will first be corroborated by calculations and then demonstrated experimentally within the scope of an on-going German strategy fund by the Hermann von Helmholtz Association (15 National Research Centres) and a project of the 5th Framework Programme of the European Union.

Hydrogen Permeatation

For the boiling water reactor, hydrogen generated during a severe accident may excessively increase the pressure in containment. Because of an insufficient concentration of oxygen (inerted atmosphere), it is hard to recombine hydrogen and oxygen. Hitachi Ltd. (Japan) also develops a hydrogen depletion system (HDS) using permeable materials [9]. Hydrogen molecules dissociate into atoms at the metal surface, and then diffuse (within) into palladium coating and hydrogen permeable material (tantalum). When hydrogen atoms pass through the permeable material, they are recombined to hydrogen gas on the surface of palladium at the opposite side.

Hydrogen Adsorption

Several devices based on hydrogen adsorption have been developed and studied. The hydrogen may be absorbed by: (1) organic compounds (ether propargyl byphenyl), (2) metallic oxides (manganese, cobalt and cooper oxides catalysed by silver or palladium oxides), and (3) unstable hydrides (pyrophoric reaction).

Oxygen Removal

The initial oxygen present in the containment atmosphere could be absorbed by pyrogallol in basic solution using spray system according to the reaction $2 C_6H_6O_3 + 3/2 O_2 + H_2O \rightarrow C_{11}H_8O_5 + CO_2 + 3 H_2O$. An other device consists in burning methane to eliminate oxygen in the containment according to the reaction $CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O$. These methods present some drawbacks, such as the use of an active system, a more important production of organic iodine, and a risk of hydrogen combustion in case of a too late activation.

Synthesis

The catalytic recombiner can be considered as the most appropriate hydrogen mitigation technique because:

1. A catalytic recombiner is a passive system without energy supply,
2. A catalytic recombiner operates under severe accident and design-basis accidents conditions,
3. A catalytic recombiner starts-up at low hydrogen concentration, well below the hydrogen LFL,
4. The recombiner physical phenomenology is well known,
5. A catalytic recombiner does not induce operational constraints in normal operation,
6. The passive autocatalytic recombiner technology is simple and does not need complex system.

The intrinsic limitations of catalytic recombiner are the hydrogen ignition risk due to catalyser surface heating and the mass transfer limited hydrogen depletion rate (which is at the same time beneficial). Other systems as mixing systems, hydrogen absorption can induce combustion and igniters could trigger local detonation. The hydrogen ignition risk is well known. The H2PAR experimental tests show that the ignition risk is above 5.5 vol. % hydrogen concentration in dry air and above 7 vol. % in presence of 10 vol. % steam [10].

Table 1 – Main Hydrogen Mitigation Systems and their Intrinsic Limitations

Method	Intrinsic Limitations
Catalytic Recombiners	Can induce combustion above 7 % hydrogen concentration (self-ignition) Mass transfer limited depletion rate
Thermal Recombiners	Active system (energy supply) + Implementation outside the containment Low hydrogen recombination rate High cost of maintenance
Ignitors	Can trigger local detonation if in wrong position (7λ) Not effective under inert conditions (steam, nitrogen enrichment)
Pre-inerting Systems	Important operational constraints under normal operation (anoxia risk)
Post-inerting Systems	Active method and complex system for technical realisation Short delay for decision, actuation and completion (0.5 h)
Mixing Systems	Active system Static ignition of combustion
Hydrogen Absorption	High cost and important quantities of getters Large uncertainties of phenomenology knowledge
Hydrogen Recombination	Large uncertainties of phenomenology knowledge
Oxygen Removal	Use of spray system and important quantities of getters Large uncertainties of phenomenology knowledge

PRESENTATION OF THE MAIN EXPERIMENTAL ACTIVITIES

This sub-section gives an overview of the experimental activities on the commercial catalytic recombiners. The presentation is limited to the facility description and an overall tests program presentation.

AECL Facilities

Different recombiners (prototypes, models in a scaled-down, commercial units) were experienced for use in commercial reactor containments using two qualification installations: the Containment Test Facility (CTF) and the Large Scale Vented Containment Facility (LSVCF) located at AECL Whiteshell research centre.

The Large Scale Vented Containment Facility is a 10 m long, 4 m wide, 3 m high rectangular enclosure with an internal volume of 120 m^3 (figure 9). This facility is constructed of 1.25 cm thick steel plates welded to a rigid frame work steel I-beams. The entire structure is anchored to a 1 m thick concrete pad. Two roller-mounted movable end walls are provided to open up the vessel for internal modifications or to move-in bulky experimental equipment when needed. The entire combustion chamber is enclosed in an insulated metal Quonset, which houses the gas analysis and hydraulic fan systems on one side and all the valves and piping on the other side. The combustion chamber can be divided into 2 or 3 compartments using structural steel partitions. Eight fans are installed in the combustion chamber to mix the gases uniformly. The design pressure is 300 kPa, with a dynamic load factor of 2.
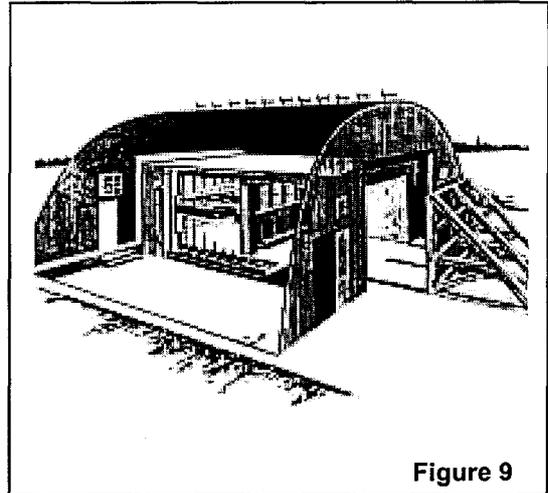

Figure 9

Qualification tests, using a commercial model (0.2 m^2 inlet), have been performed in the Large Scale Vented Containment Test Facility with environmental conditions simulating nuclear reactor environment (1995-1998). The main studied items were: (1) functional tests for self-start threshold and capacity, (2) ageing (gamma radiation with a total integrated dose of 370 kGy and thermal), (3) LOCA hydrogen transient bounding CANDU-6 and CANDU-9 cases (1-6 % vol. H$_2$), (4) chimney and water sprays with chemicals (hydrazine, boric acid), and (5) combustion products resulting from cable burns (hydrochloric acid, chlorine).

Battelle Facilities

The Batelle Model Containment (BMC) is a small-scale German nuclear power plant (multi-compartment) that is composed by a cylindrical containment model 9 m high with a diameter of 12 m (internal free volume configurable from 210 to 625 m^3) (figure 10). The facility is composed by a central cylindrical room, a dome region, a ring room and annular compartments at two different levels between the ring room and the central room, which can be interconnected through set-ups of overflow openings [11].

Tests Gx 4-7 investigated the performance and effect of the Siemens catalytic recombiner in a multi-compartment geometry (five rooms) under conditions of stratified and homogeneous steam-air-hydrogen mixtures. Test results showed a dependence of the vertical mixing of hydrogen in the atmosphere to the existing density stratification and to the position.
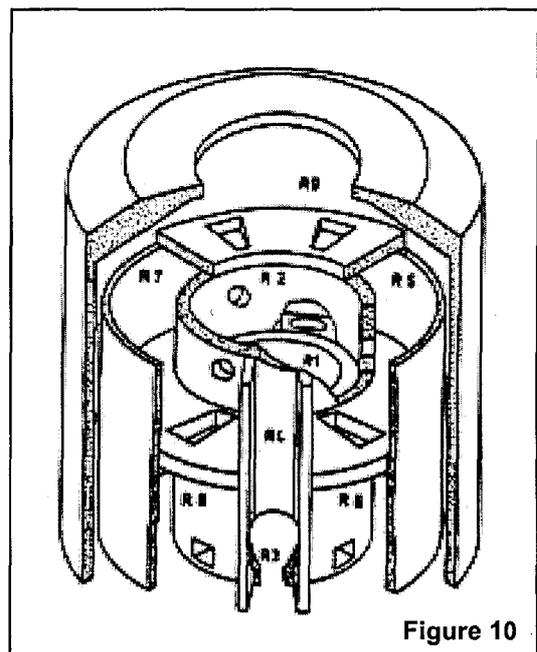

Figure 10

A second experimental program (1994-1998) was performed within the 4th European Framework Program on safety on nuclear fission with three catalytic recombiners installed inside the 640 m³ multi-compartment vessel at different distances from the steam hydrogen release site. The objective of the Zx-tests was to investigate the interactions of some catalytic recombiners and a steam-air-hydrogen atmosphere [12].

Sandia Facility

The Surtsey vessel is an American Society of Mechanical Engineers (ASME)-approved steel pressure vessel with a current working internal volume of 99 m³. Twenty 30.5 and 61 cm instrument penetration ports allow steam, noncondensible gas, water, electrical, and video service into and out of the vessel (at sic different levels around the perimeter of the vessel). The vessel walls and heads are 1 cm thick and covered with at least 10 cm of fibreglass insulation [13].

The Surtsey vessel has a cylindrical shape with removable, dished heads attached to both ends (10.3 m high and 3.6 m diameter). The Surtsey vessel has a maximum allowable working pressure of 10 bar at 533 K (260 °C).

The catalytic recombiner is located at the vessel centreline, with the recombiner inlet at about 4.5 m from the vessel dome. At about 1 m below the catalytic recombiner inlet exist horizontal and vertical I-beams, which previously supported a false floor above the midline elevation in the Surtsey vessel (figure 11).

The experiments determined the hydrogen depletion rate of a catalytic recombiner in the presence of steam, and also evaluated the effect of scale (number of cartridges) on the PAR performances.
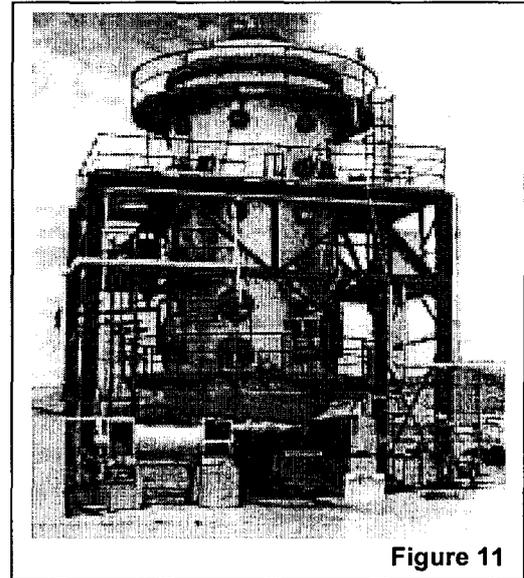

Figure 11

H2PAR Facility

H2PAR is a facility managed by the French Institute for Nuclear Protection and Safety (IPSN), and is located at CEA Cadarache research centre (France). The objectives of the H2PAR program are to characterise the behaviour of catalytic recombiners under conditions typical of those expected during a severe accident in a PWR, and to understand the physics and chemistry that govern the efficiency of the devices [14].

The facility is made of a double terphane (polyester film) vessel. The internal volume is about 8 m³ for a diameter of 2 m. This vessel is fixed on a stainless steel plate. A double plastic vessel is needed because the interstitial area is heated by thermal resistance located on the plate to allow thermal insulation of the inner containment. The inner containment confines the gaseous mixture and the aerosols, and encloses a heated 50 litres water volume, which allows to control the atmosphere steam content (figure 12). An induction furnace, a recombiner and a measuring device are set up inside the vessel. Non-radioactive elements were introduced and heated until to 2900°C (close to the UO_2 melting temperature).
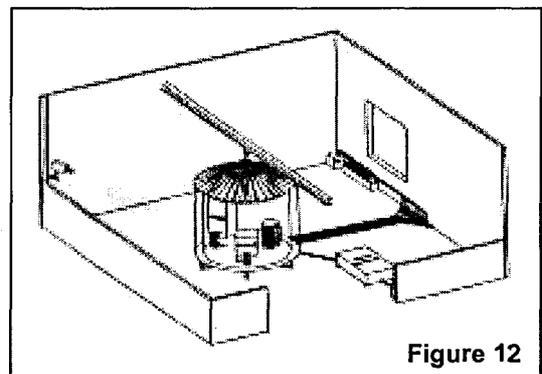

Figure 12

The test program comprised four series [8]: (1) preliminary tests whose objective was to qualify the source of aerosols, (2) tests with recombiner without aerosols (reference), (3) operational tests of the recombiner in presence of aerosols, and (4) tests for studying the risk of ignition starting from the recombiner.

KALI H2 Facility

KALI H2 facility is located at CEA Cadarache research centre (France). The KALI vessel is a 15.6 m³ steel cylindrical vessel (4.6 m high, 2.1 m diameter), and has a maximum allowable working pressure of 12 bar at 473 K. The experimental tests are restricted to a 10 % vol. hydrogen concentration in dry air.

The KALI facility allows to simulate the thermohydraulic conditions of severe accident or design-basis accident atmosphere and to reproduce mixtures with air, steam and hydrogen. The facility is also equipped with carbon monoxide injection system, cold water spray system, and mixing fan inside the vessel to have homogeneous mixture (figure 13).

The items that were investigated are: (1) the effect of water spray, (2) the analytical study of Siemens and NIS recombiners both in design-basis accident and in severe accident, (3) the self ignition induced by recombiner (in dry/wet atmospheres), (4) the effect of long time (one week) thermal degradation of electric cable fire, (5) the recombination rate and the possibility of self-ignition, (6) the simulation of catalytic recombiner thermal power, and (7) the measurement of the gas velocity.
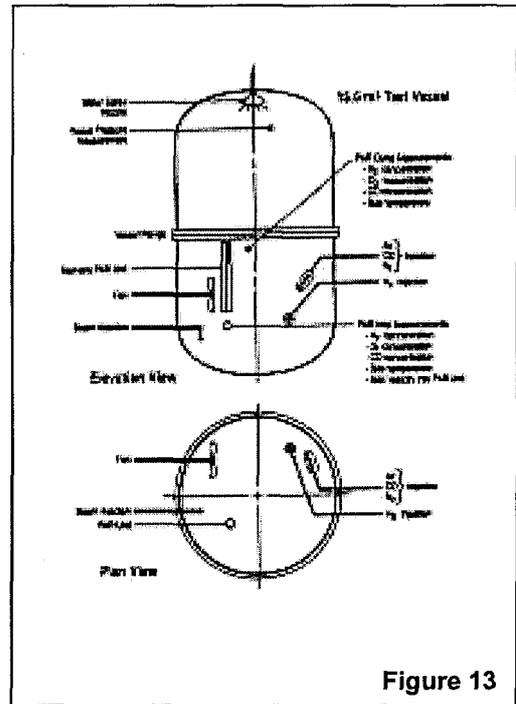

Figure 13

PRESENTATION OF CATALYTIC RECOMBINER QUALIFICATION

A passive autocatalytic recombiner must be designed to operate at nominal recombination capacity in all accidental conditions (not only design-basis accidents but also severe accidents). This device has also to withstand internal and external hazards, and however to be able to ensure the nominal performances after internal and external hazards. At last, a catalytic recombiner must not induce an additional combustion hazard during operation, and normal operation in nuclear power plant must not affect the intrinsic recombiner performances for a later use (effects of ageing).

A passive autocatalytic recombiner must be compliant with nine major design requirements [9]:

1. Have a low self-starting threshold hydrogen concentration (2-3 % vol.),
2. Be active in low oxygen concentrations (pre-inerting BWR, post-inerting submarine reactors),
3. Be active at low temperatures (from 15-50 °C depending on the applications),
4. Withstand high catalyst temperature (700-800 °C),
5. Be active in pressurised atmosphere (several bar),
6. Be active in saturated steam or with high wetness level (break, spray system),
7. Be insensitive to the carbon monoxide (due to corium-concrete interaction after vessel rupture),
8. Accept up to 400-500 kGy absorbed radiation dose,
9. Have a long lifetime (equal to those of nuclear power plants),
10. Be insensitive to poisoning during accident conditions:

   - Iodine and aerosols produced by core melting (both radioactive and non-radioactive isotopes),
   - Organic iodine produced by chemical reactions between molecular iodine and paints,
   - Fire products as carbon, sulphur, hydrochloric and sulphuric acids,
   - Boric acid present in primary water and released with steam.

Effect of Hydrogen Concentration

The effect of hydrogen concentration is to increase the recombination rate proportionally. At low hydrogen concentration (design-basis accident), the self start is spontaneous at 1 % H_2 and 25°C for AECL device, 2 % H_2 and 30°C for NIS and Siemens devices. Catalytic recombiners tested at low hydrogen concentration start-up spontaneous in dry condition and with delay in wet condition, depending on wet-proofing. At high hydrogen concentration (8-10 % vol.), the start up is spontaneous for all recombiners.

Effect of Oxygen Concentration

The boiling water reactors are often pre-inerted with an oxygen concentration below 4 % vol. The behaviour of catalytic recombiners in inerted conditions was tested in KALI H2 facility. The catalytic recombiners tested at low oxygen concentration representative of pre-inerted BWR start-up after a 1-5 minutes delay and reduces the oxygen concentration below 2 %. However, they have often tested under high hydrogen concentration which is representative of severe accident conditions (8-10 %). It should be tested under DBA conditions: around 6 % oxygen concentration and 4 % hydrogen concentration.

Effect of Containment Temperature

The effect of containment temperature have been tested for a large temperature range from 15 °C to 100 °C. The recombination rate decreases with increasing temperature. The increasing temperature decreases the molar density of oxygen and hydrogen in contact with the catalyser sites. This decreasing capacity could reach from 10 to 20 %. The tests carried out at hot temperature in wet conditions (severe accident) showed that all recombiners started up immediately or with short delay (few minutes) while their performance capacity was reduced by the effect of containment temperature. The tests carried out at cold temperature after a slow refrigeration (design-basis accident) showed that all recombiners kept an acceptable efficiency.

Effect of Catalyst Temperature

The catalyst bed must withstand very high temperatures (700-800 °C) without degradation (superheating due to the exothermic reaction of hydrogen and oxygen recombination).

Effect of Pressure

The pressure increasing is favourable for the catalytic recombiner efficiency. However, the effect of pressure is to lowly increase the hydrogen recombination rate (less than the law of the absolute gas).

Effect of Steam

All catalytic recombiners were tested in wet conditions. KALI H2 tests showed that the steam increased the recombination rate at a given initial pressure more than enough to compensate for the reduction due to temperature increase (mass density decrease). However, it is necessary to protect catalytic recombiner from spray because of the recombination rate decrease (or stops) until the catalyst dries.

Effect of Carbon Monoxide

Carbon monoxide oxidises on platinum or palladium catalysts in the presence of oxygen according to the exothermic reaction $CO + 1/2\ O_2 \rightarrow CO_2$ ($\Delta H = - 284$ kJ/mol). Oxidation of carbon monoxide on the catalyst may result in partial inhibition of the catalyst with respect to oxidation of hydrogen, since carbon monoxide molecules occupy some hydrogen adsorption sites. At low temperatures, CO is easily adsorbed on active sites in the catalyst and inhibits the capacity of the catalyst to oxidise hydrogen. The carbon monoxide on catalyst surfaces is consumed as soon as the temperature increases.

For oxygen-rich pressurised water reactor conditions, CO increases the PARs recombination rate, probably due to the exothermic reaction of carbon monoxide and oxygen to form carbon dioxide. For low-oxygen boiling water reactor conditions, CO delays recombination significantly, but only when oxygen concentrations fell below about 2 vol. % [15].

Effect of Ageing

The catalytic recombiners are constructed of metals and other materials whose physical properties do not change under long term exposure to operating temperature and radiation environments in containment. To assess the ageing effects on the catalytic recombiners, the nuclear power plant utilities must test periodically their efficiency of their devices. Each site in Belgium is provided with a Transportable In-Service Inspection Equipment (TIIE) to perform the in-service inspection [16].

Effect of Radiation

The effects of radiation on the performance of catalytic recombiners must be addressed. Conventionally, this is done by subjecting a component containing one or more non-metallic sub-components to radiation prior to qualification performance testing. Catalytic recombiners consist mainly of metals and ceramics, which are known to be unaffected by typical accident doses. However, for any hydrophobic coating that must be relied upon to allow sufficiently prompt recombiner start-up when it is wetted, radiation effects will have to be addressed to ensure that the organic material in the hydrophobic coating does not lose its ability to perform its safety function (SF) prior to the time during an accident that the function is needed.

Effect of Poisoning (Normal Operation)

A deposit on the active catalyst may damage the catalytic recombiner performances. The poisoning risk in normal operation is essentially due to the dust. However, organic vapours (released during painting work in the containment) and oils (used and present in the containment) may also contribute to the degradation of the catalyst plates. The implementation of a policy of maintenance and in-service inspection is also necessary to avoid the negative effects of ageing and poisoning.

Effect of Poisoning (Accidental Conditions)

For any type of accidental sequence, some poisons are generated: (1) the boric acid released from the primary circuit or injected in containment by spray system, (2) the methyl iodine produced by chemical reaction between molecular iodine and paints, (3) the iodine and aerosols released from the molten core, and (4) the cables fires induced by hydrogen combustion or electrical short-circuit, (5) thermal insulation and radiological protection materials fragments produced by irradiation effect, fluid jet, pipe whip, hydrogen burn.

Concerning the effect of a cables fire, the effect of pre-exposure of a catalytic recombiner to a conservatively high amount of fumes from an electrical cable fire (US cable fire) is to reduce the recombination rate on the order of 10 percent [15].

HYDROGEN IGNITION RISK INDUCED BY CATALYTIC RECOMBINERS

A chemical recombination of hydrogen and oxygen is extremely exothermic and brutal. Ignition tests were performed in AECL, BMC, KALI H2 and H2PAR facilities. EdF/EPRI tests performed in the KALI H2 facility showed that hydrogen inlet concentration of 7 % vol. in dry air led to ignition for catalytic recombiners. The conclusions [14] are that a generalised ignition may appear in dry air between 5.5 and 6.8 % of hydrogen molar fraction, and that a generalised ignition may appear at 9 % vol. steam for a 8.5 % hydrogen molar fraction (figure 14).
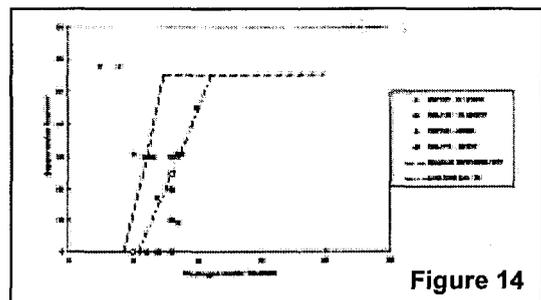
Figure 14

It is also possible to draw the following conclusions: (1) there is no risk of generalised ignition with a hydrogen concentration below 5.5 % in air with less than 10 % steam, (2) there is no hydrogen combustion hazard induced by catalytic recombiner in design-basis accident because the hydrogen release is relatively slow and the recombiners start up before reaching hydrogen flammability, (3) in case of severe accident, the hydrogen combustion could be induced both by recombiners and by other ignition sources such as electrical short circuit, auto-ignition gas (from 180°C).

This risk is accepted by most of safety authorities (SA), which consider that the safety improvement due to passive autocatalytic recombiner against hydrogen combustion counterbalances the hydrogen combustion hazard induced by such device.

RECOMBINER MODELLING

Numerical models were developed to simulate the behaviour of catalytic recombiners subjected to accidental conditions. The main objectives are: (1) to evaluate the recombination rate in any accidental conditions, (2) to give a tool to optimise the recombiner design, and (3) to give a subroutine to containment codes to determine the optimal number and location of the catalytic recombiners inside the containment. Three different approaches for taking into account the presence of passive autocatalytic recombiners in a given containment are possible : (1) the empirical model or correlation for module hydrogen recombination rate, (2) the theoretical multi-dimensional model of internal recombiner behaviour, and (3) the global approach that integrates the importance of the local thermal hydraulic conditions.

Empirical Model (Correlation)

It is based on experimental measurements and gives an approximation of the global hydrogen recombination rate according to global variables : hydrogen concentration, oxygen concentration, atmosphere temperature, total pressure, and moisture conditions. Specific constants or complex normalisation function allow a good agreement with the experiments. The main drawbacks of this particular approach are that the environment of the catalytic recombiners is neglected, and that the validation of the correlation is strictly limited to the field covered by the experiments.

Such an approach is very insufficient because it does not take into account the physical phenomena inside the catalytic module (local flow, heat generation) and the thermalhydraulic processes inside the reactor containment (global natural convection flow generated by the catalytic recombiner that lead to a continuous transport of hydrogen from the remote source to the catalytic module, turbulent flow induced by the break, and probable gas-stratification and local hydrogen over-concentrations). The majority of the catalytic recombiner designers have developed empirical models (table 2).

Table 2 – Empirical Models for Catalytic Recombiners

	Empirical Model	Constants
AECL	$r \text{ (kg/h)} \cong 0.20 \times [H_2] \times P/P_0 \times (T_0/T)^{1.5}$	$P_0 = 1 \text{ bar } T_0 = 293 \text{ K}$
NIS	$r \text{ (kg/s)} \cong 1.134 \times C_{H2}^{1.307} \times (P/RT)$	$R = 8.31 \text{ J/kg.K}$
Siemens	$r \text{ (g/s)} \cong [H_2] \times (k_1 \times P/P_0 + k_2)$	$P_0 = 1 \text{ bar}$

$[H_2]$ Hydrogen concentration in vol. % wet basis
C_{H2} Hydrogen volumetric concentration inside the recombiner in m^3/m^3
k_1 / k_2 Constants depending on the recombiner model

Theoretical Model

It is based on a mathematical approach of the different physical processes that take place inside the catalytic module. There are two kinds of theoretical models along with the initial hypothesis : (1) the reaction kinetics are dominant and control the hydrogen recombination, and (2) the transport phenomena are prevailing. The main purposes of a theoretical model are : (1) to assess the hydrogen recombination rate in any accidental sequence, (2) to give a tool to optimise the recombiner design, and (3) to give a subroutine to containment codes to determine number and best location of the catalytic recombiners in the containment (optimal efficiency of the hydrogen mitigation strategy). In the last years, several theoretical models were developed to simulate the « internal » chemical and physical phenomena inside catalytic recombiners [17-21].

Global Approach

This approach includes the thermalhydraulic impact of the recombiner on the containment atmosphere. The hydrogen depletion rate of a catalytic recombiner is affected by the local thermal hydraulic conditions (mixing inside the containment) during an accidental sequence. To analyse performance of a catalytic recombiner, it is important to take into account the local hydraulic conditions including the natural convection flow caused by the catalytic reaction heat. The gas flowing through a catalytic recombiner heats up due to the exothermic reaction between hydrogen and oxygen, which takes place inside it. This is the reason why a natural gas circulation starts linked to the recombiner in the partially confined control volume around it. Such a circulation assures a continuous hydrogen-oxygen supply and influences the power supplied by the recombiner that has in turn a feedback on the natural circulation.

Because of the coupled action between recombination reaction and natural convective flow, it is essential to develop a numerical computer model by coupling two « elementary » models in order to simulate with a good agreement the catalytic recombiner impact inside the containment of a nuclear power plant : (1) the first model or « internal » model that simulates the recombination reactions, the thermodynamic and fluid-dynamic gas exchanges inside the recombiner, and (2) the second model or « external » model that simulates the thermalhydraulic gas exchanges inside the control volume (close environment of the recombiner), after the gaseous mixture has left the device and before entering it again (figure 15).

Several attempts of coupling these both aspects have been made the last years (table 3).
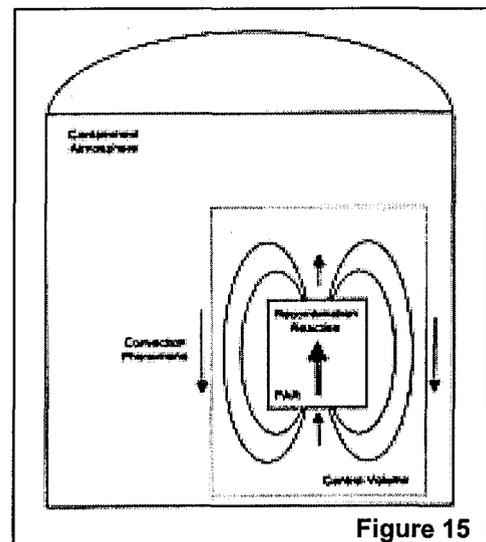

Figure 15

Table 3 – Global Approach

	Institution	Country	Internal Model	External Model		Qualification/Applications
G. Avakian	CEA/IPSN	France	0-D	TONUS	3-D	
M. Heitsch	GRS	Germany	3-D (r, θ, z)			
M.A. Movahed	Siemens	Germany	Empirical	WAVCO	LPC	BMC (Jx-7)
J. Rohde	GRS	Germany	1-D (z)	RALOC	LPC	BMC (Gx4, Gx6 tests)
P. Royl	FZK	Germany	Empirical	GASFLOW	3-D	Biblis A, Neckar II (German PWR)
F. Fineschi	DCMN/ENEL	Italy	Empirical	HOCRA	0-D	Westinghouse scenarios HYD1-3
F. Fineschi	DCMN	Italy	1-D (z)	PARCO	0-D	BMC (Zx2, Zx3, Zx4, Zx8 tests)
M. Tahara	Toshiba	Japan	2-D (r, z)	STRA-CD	3-D	BMC (MC-1B test)

Limits and Complementary Needs

Nowadays, a global methodology based on computer codes for assessing the hydrogen hazard in a nuclear power plant and the efficiency of a hydrogen mitigation strategy based on catalytic recombiner, does not exist. An adequate coupling of internal model (catalytic recombiner) and external model (containment atmosphere) is not yet available. A number of limits and complementary needs have been identified: (1) the no-integration of dimensional internal model about recombiner in lumped parameter or three-dimensional codes used for H2 distribution inside the containment, (2) the absence of benchmark about the computer approach of the hydrogen hazard in presence of catalytic recombiners, and (3) the absence of modelling about the probable ignition phenomena inside the catalytic recombiner (hot catalyst plates), the degradation or destruction of the recombiner, and the propagation of the combustion phenomena outside the recombiner.

NATIONAL APPROACHES FOR IMPLEMENTING CATALYTIC RECOMBINERS

The choice of a hydrogen mitigation system for a given nuclear power plant depends on many parameters like the hydrogen sources inventory (global amount and hydrogen release rate), the considered accident sequences (design-basis accident, severe accident), the design and the dimensions of the containment, and the hydrogen criteria.

In order to bring out the main axes of a common practice for implementing passive autocatalytic recombiners in a nuclear power plant (or in an industrial installation), the workgroup has been carrying out step-by-step: (1) state of the art on the implementation of hydrogen mitigation measures in countries using the nuclear energy, (2) presentation of the national approaches for implementing catalytic recombiners on the basis of a structured questionnaire, and (3) definition of an optimal methodology for designing a hydrogen control system (HDS) based on the use of passive autocatalytic recombiners.

Status of Implementation of Hydrogen Mitigation Measures

The hydrogen risk mitigation strategy could be carried out by one or a combination of different techniques: (1) deliberate ignition of the mixture, (2) recombination of hydrogen by catalytic recombiner, (3) removal of oxygen by pre-inertisation, (4) dilution of the atmosphere by post-accidental injection of inert gas, and (5) dilution of the atmosphere by increase of the containment volume.

The design of the containment is an important parameter for the mitigation strategy choice: (1) most of small containments as Mark I and Mark II boiling water reactors are pre-inerted, (2) Mark III, multi-units CANDU, pressurised water reactors with ice condenser are equipped with ignitors, and (3) pressurised water reactors with large containment will be equipped with catalytic recombiners.

The main tendencies for the hydrogen hazard mitigation are: (1) implementation of catalytic recombiners in existing nuclear power plants in European Union and Canada for design-basis accident and beyond-design-basis accident, (2) implementation of catalytic recombiners in existing nuclear power plants in East Europe and United States of America only for design-basis accident, and (3) pre-inerting of boiling water reactors in Japan, United States of America and Sweden completed by igniters in Japan (annexe 1).

National Approaches for Implementing Catalytic Recombiners

It exists different approaches for implementing passive autocatalytic recombiners in existing nuclear power plants. Some countries that have chosen passive autocatalytic recombiners as hydrogen mitigation strategy, have been selected and subjected to the same questionnaire: Belgium, Canada, Finland, France, Germany, Netherlands, Japan, and United States of America. The table in annexe 2 gives a synthetic overview of the national approaches for implementing catalytic recombiners.

The passive autocatalytic recombiners implementation is governed by: (1) the hydrogen production, (2) the hydrogen distribution, (3) the assessment of catalytic recombiners location and number, and (4) the catalytic recombiners management.

Methodology for Implementing Catalytic Recombiners (Existing Nuclear Power Plants)

It therefore exists different approaches for implementing recombiners in existing nuclear power plants, but, with important common points. In most of countries, except the United States of America and Earthen European Countries, catalytic recombiners were implemented nuclear reactors to mitigate both the design-basis accidents and the severe accidents. The catalytic recombiners implementation is governed by: (1) the hydrogen production, (2) the hydrogen distribution, (3) the hydrogen recombination and combustion, and (4) the catalytic recombiners management.

Hydrogen Production: In severe accident, the hydrogen production is characterised by the chemical reaction between fuel cladding (zirconium) and steam, the other hydrogen sources as the radiolytic decomposition of water being negligible at short term. However, all countries do not take into account the global oxidation of zirconium because the severe accidents analysis is led with a « best estimate » approach. The advantage of the major assumption of 100 % zirconium oxidation would be to cover the sequences of hydrogen production during core re-flood (large uncertainties concerning hydrogen production during this phase). The conservative assumption of 100 % zirconium oxidised leads to over-design the recombination capacity, what could pose a problem of expensive cost and implementation in nuclear power plants. The accidental sequence taken into account in most of countries is the small loss-of-coolant accident (LOCA) with failure of emergency core cooling system (ECCS) to assess hydrogen production by zirconium oxidation.

Concerning hydrogen production, the second issue is the core-concrete interaction (CCI), which follows the vessel breach. The numerical model predicting the hydrogen production is not yet validated. There is still a need to develop numerical models for predicting hydrogen production due to core-concrete interaction.

Hydrogen Distribution: The mixing of gases depends on some parameters as multi-compartment geometry, temperature, physical properties, convective flow, hydrogen release rate. The use of an assumption of homogeneous hydrogen concentration is an important economy of calculations. Although such assumption is not representative, the uncertainties concerning the hydrogen distribution knowledge can be compensated using a low hydrogen concentration limit for designing catalytic recombiners (Belgium approach). Belgian nuclear power plants utilities used a safety limit of 5 % for hydrogen concentration.

German nuclear power plants utilities adopted another approach. They used lumped-parameter codes (LPC) and three-dimensional (3-D) codes to assess hydrogen distribution. The GKN-2 nuclear power plants utilities consider that lumped-parameter codes are sufficient for further analysis [22]. Moreover, the global validation of three-dimensional computer codes used for hydrogen distribution calculation is not yet obtained, and the use of such codes is more expensive than lumped-parameter codes.

Assessment of Catalytic Recombiners Location and Number: Concerning recombiners implementation in the existing nuclear power plants, the engineering judgement is often used because catalytic recombiners can only be implemented in available location that does not forbid the access to other components for maintenance and in-service inspection. Different criteria may be used to implement catalytic recombiners: (1) hydrogen sources location, (2) accessibility of catalytic recombiners to allow maintenance and in service inspection, (3) accessibility to other components particularly those related to safety systems, and (4) protection of catalytic recombiners against internal hazards induced by the initial accident (pipes whip, fluid jet, missiles, floods).

The hydrogen recombination depends on the catalytic recombiners number and capacity, and their locations. The number of recombiners was often calculated considering the adiabatic isochoric complete combustion (AICC) pressure less than the containment failure pressure (design pressure) or an average hydrogen concentration (e.g., less than the low limit of fast deflagration). For example, the Belgian nuclear power plants utilities used the safety limit of 5 % for hydrogen concentration to assess the catalyst surface. And, the Belgium safety authorities recommended to increase this surface size of twenty per cent to consider the hydrogen distribution heterogeneity.

On the basis of H2PAR and KALI H2 ignition tests results, a value of 7 % vol. for averaged hydrogen concentration (considering steam presence) seems to be reasonable to design the recombiners number. If a less value of hydrogen concentration is taken into account, it would be a conservative approach, where the positive effect of steam as inert gas would be neglected. The number of passive autocatalytic recombiners would be increased without perhaps improving sensitively the safety margins and with generation of problems for maintenance and in-service inspection due to difficult access to catalytic recombiners and other safety components.

Catalytic Recombiners Management: It can be noted that the support of passive autocatalytic recombiners are often designed to withstand earthquake, particularly safe shutdown earthquake. Finally, it is interesting to decrease the application of the single failure criteria to passive autocatalytic recombiners.

Catalytic recombiners being used to mitigate both the design-basis accidents and the severe accidents, they have therefore to consider as safety systems of the third level of defence in depth, which protect the third barrier from hydrogen explosion in design-basis condition. The single failure criteria (SFC) should be applied to the catalytic recombiners and they have to manage as safety systems concerning their maintenance and the in-service inspection.

In addition, it is important to implement a policy of PARs management in the nuclear power plants. The catalytic recombiners should periodically be tested in order to check their efficiency. The transportable in-service inspection equipment (TIIE) has be designed to enable reproducible condition simulating the real recombiner operating conditions. The TIIE is located in an easy transportable rack and essentially consists of test gas supply connected with pressure reducing set, test gas heating device, insulated heatable test receptable with support for a catalytic plate, and flow and temperature measurement. The start of the catalytic reaction is detected by the temperature increase of the catalytic plate surface. At last, the nuclear power plants utilities should planned a periodic visual inspection of the catalyst beds.

Methodology for Implementing Catalytic Recombiners (New Nuclear Power Plants)

In the design process, consideration is given to utilisation of passive safety systems (PSS) based on natural phenomena (natural convection, gravity). Several projects of evolutionary plants have been undertaking the last ten years: simplified boiling water reactor (SBWR), SWR 1000, European pressurised water reactor (EPR), CANDU-9, and American advanced light water reactor (AP600). Most of projects are incorporating passive safety features to protect the third barrier from hydrogen combustion in DBA and BDBA conditions.

The evolutionary boiling water reactor concepts use inerting of the containment to prevent deflagration and detonation of combustible mixtures of hydrogen and oxygen [23]. This hydrogen hazard mitigation strategy is often complained by catalytic recombiners to eliminate oxygen produced by water radiolysis at long term.

In new pressurised water reactors, catalytic recombiners are incorporated in the design to limit the hydrogen concentration during accidents. Moreover, the containment building is sometimes designed to withstand a certain level of hydrogen explosion. For example, EPR containment building shall be designed to withstand a global hydrogen deflagration (melt accident) [24]. The hydrogen production stable is carried out taking into account an oxidation of 100 % zirconium and core-concrete interaction with the help of qualified codes.

It is planned for several advanced reactors (SBWR, EPR, AP600, CANDU-9) to implement a dual strategy based on ignitors and catalytic recombiners because of a probable risk of local hydrogen over-concentration, which could induced a local fast deflagration. The use of this dual strategy addresses several issues: (1) the capacity of igniters to operate in high hydrogen concentrations (above 8 % vol.), (2) the capacity of igniters to operate in inerted condition (steam), (3) the delayed start up time of igniters compared with recombiners, (4) the preferential ways of hydrogen flows to the igniters rather than the recombiners.

CONCLUSIONS

The present study shows that the catalytic recombiner is the most adequate system to mitigate the hydrogen hazard in a nuclear power plant because of its efficiency both in design-basis accident and in beyond-design-basis accident, its passive characteristic, its well known technology (chemical and physical processes), its well defined maintenance, and its low cost compared with other hydrogen mitigation systems.

At the present time, it can be considered that recombiner designers have achieved their development: they have been successfully tested their devices in design-basis accident and severe accident conditions in their own facilities or in independent facilities. Few complementary experimental tests about poisoning effect or for simulating design-basis accident conditions in an inerted boiling water reactor, should be performed to complete the qualification.

Numerical models on the catalytic recombiner behaviour have been developed, and their integration in global computer codes are in progress. However, these models are insufficient because they can not simulate the probable hydrogen ignition phenomena inside the catalytic recombiner (hot catalyst plates), the degradation or destruction of the device, and the propagation of the combustion wave outside the recombiner.

To conclude, a first inventory of the national practices for implementing passive autocatalytic recombiners in nuclear power plants makes it possible to define or outline a common approach from the hydrogen sources quantification to the catalytic recombiner management. The development of this common approach will be the subject of the second part of the project with the writing of a handbook guide.

Annexe 1: Status of Implementation of Hydrogen Mitigation Measures in Different Countries

Country	Plant	Hydrogen Mitigation Measure(s)	Implementation/Preparation
Belgium	Doel 1-4	Catalytic Recombiners (Siemens)	Available in All Nuclear Power Plants
	Tihange 1-3	Catalytic Recombiners (Siemens)	
Finland	Loviisa	Ignitors (+ AECL Catalytic Recombiners)	In Preparation
France	PWR (57)	Catalytic Recombiners	Licensing Procedure in Progress
Germany	PWR (13)	Catalytic Recombiners (NIS, Siemens)	Already Implemented (in the Licensing Procedures)
	BWR (2)	Partial Inerted + Catalytic Recombiners (NIS)	Implementation Completed
Netherlands	Borssele	Catalytic Recombiners (Siemens)	Implementation Completed
Spain	Trillo 1	Catalytic Recombiners (German solution)	Preparation of a Decision-Making (in Progress)
Sweden	Ringtails	Filtered Venting	Investigations in Progress
Switzerland	BWR Mark I	Inerting (Nitrogen)	
	BWR Mark III	Igniters	Mixing under Starts Study
	PWR		
Bulgaria	Kozloding 5-6	Catalytic Recombiners (Siemens)	Implantation in Progress (for DBA)
Czech Republic	Dukovany 1-4	Catalytic Recombiners (Siemens)	Implementation Completed (for DBA)
	Temelin 1-2	Catalytic Recombiners (Siemens)	Implementation in Progress (for DBA)
Hungary	Paks 1-4	Catalytic Recombiners (Siemens)	Implementation Completed (for DBA)
Russia	Kalinin 1, 3	Catalytic Recombiners (Siemens)	Implementation in Progress (for DBA)
Slovakia	Bohunice	Catalytic Recombiners (Siemens)	Implementation Completed (for DBA)
	Mochovic		
Canada	CANDU-9	Catalytic Recombiners (AECL)	Part of the New Reactor Design
	CANDU single unit	Catalytic Recombiners (AECL)	Implementation in Preparation
	CANDU multi-unit	Igniters + Mixing System	Catalytic Recombiners for the Long-Term (in Discussion)
USA	ALWR (AP600)	Catalytic Recombiners (NIS) + Ignitors	Generic Licensing in Progress
	Old PWRs/BWRs	Inerting + Catalytic Recombiners (NIS)	Thermal → Catalytic Recombiners for DBA (in Preparation)
Japan	OHI 1-2 (PWR)	Glow-Plug (Ice-Condenser Containment)	Installation of 34 Igniters (in Preparation)
	Others PWR (21)	No Strategy	Dilution of Hydrogen (Large Volume) ?
	BWR (27)	Inerting	Catalytic Recombiners Planned in Future BWRs

Annexe 2: National Approaches for Implementing Catalytic Recombiners in Nuclear Power Plants

	DBA	BDBA	Class of Accident Sequence	Hydrogen Production Core Uncovered	Code	Hydrogen Distribution	PARs System Definition	Location
Belgium	×	×	Small LOCA + ECCS Failure	Best Estimate	STCP	Homogeneous Mixture	$[H_2]^{Average} < 5\%$ $+\ 20\%$ Surface (Margin)	Expert Judgement
Canada	×	×	LOCA + ECCS Failure	Best Estimate	MELCOR	3-D (GOTHIC)	$[H_2]^{Average} < 8\%$ $P^{AICC} < P^{Ultimate}$	Expert Judgement + GOTHIC verification
Finland	×	×	LOCA + ECCS Failure	100 % Zr	Enveloping H2 Releases	LPC	$[H_2]^{Average} < 9\%$ $P^{AICC} < P^{Design}$ (3.25 bar)	Expert Judgement
France	×	×	Small LOCA + ECCS Failure Loss of SG + ECCS Failure + (2)	Best Estimate	MAAP	LPC	$[H_2]^{Average} < 8\%$ $P^{AICC} < P^{Design}$ (6 bar)	Expert Judgement
Germany	×	×	Loss of Feed Water Supply LB LOCA (Surge-Line LOCA) SB LOCA without PDE (3) SB LOCA with PDE (3)	Best Estimate	MELCOR	LPC (RALOC) 3-D (GASFLOW)	$[H_2]^{Local} < 10\%$	Use of Codes
Netherlands	×	×	LOCA + ECCS Failure	Best Estimate		LPC	$P^{AICC} < P^{Design}$	Expert Judgement
USA	×	(1)		100 % Zr (1)	MAAP MELCOR	Single Failure Criterion (DBA)		

(1)   only for future nuclear power plants
(2)   late open of primary pressurizer depressurisation

REFERENCES

[1]   M. Berman, J.C. Cummings, « Hydrogen Behaviour in Light Water Reactor », Nuclear Safety 25-1 (1984) 53-74

[2]   F. Fineschi, M. Bazzichi, M. Carcassi, « A Study on the Hydrogen Recombination Rates of Catalytic Recombiners and Deliberate Ignition », Nuclear Engineering and Design 166 (1996) 481-494

[3]   W.A. Dewit, G.W. Koroll, J. Loesel Sitar « Hydrogen Recombiner Development at AECL », Workshop on the Implementation of Hydrogen Mitigation Techniques, Winnipeg, Canada, May 13-15, 1996

[4]   F. Ferroni, A.K. Chakraborty « Design Comparison of Devices for the Catalytic Removal of Hydrogen », International Conference on Nuclear Containment, Cambridge, United Kingdom, September 23-24, 1996

[5]   T.K. Blanchat, A. Malliakos, « Analysis of Hydrogen Depletion Using a Scaled Passive Autocatalytic Recombiner », Nuclear Engineering and Design 187 (1999) 229-239

[6]   B.A. Eckardt, N. Losch « Passive Autocatalytic Recombiner Systems: Design, Qualification and Implementation », 26th Annual SNE Meeting, Leon, Spain, October 4-6, 2000

[7]   M.P. Sherman, et al. « The Behaviour of Hydrogen During Accidents in Light Water Reactors », NUREG CR-1561, SAND80-1495, R3, 1980

[8]   P. Bröckerhoff, W. von Lensa, E.A. Reinecke « Innovative Devices for Hydrogen Removal », Nuclear Engineering and Design 196 (2000) 307-314

[9]   K. Yoshikawa, S. Yamanari, Y. Yoshinari « Development of the Hydrogen Depletion System for Severe Accident Using Hydrogen Permeable Material », 7th International Conference on Nuclear Engineering, Tokyo, Japan, April 19-23, 1999

[10] P. Rongier, E. Studer, J.C. Sabroux, D. Leteinturier, M. Petit, M. Durin « Passive Autocatalytic Recombiner Testing in H2PAR », CSARP Meeting, Albuquerque, New Mexico, May 3-6, 1999

[11] P. Royl, W. Breitung, J.R. Travis, H. Wilkening, L. Seyffarth « Simulation of Hydrogen Transport with Mitigation Using the 3D Field Code Gasflow », 2nd Meeting on ARS, Orlando, Florida, June 1-5, 1997

[12] OECD/NEA Group of Experts « SOAR on Containment Thermalhydraulics and Hydrogen Distribution », NEA/CSNI/R(1999), June 1999

[13] T.K. Blanchat, A. Malliakos « Testing a Passive Autocatalytic Recombiner in the Surtsey Facility », Nuclear Technology 129 (2000) 356-373

[14] E. Studer, M. Durin, M. Petit, P. Rongier, J. Vendel, D. Leteinturier, S. Dorofeev « Assessment of Hydrogen Risk in PWR », IPSN/GRS Eurosafe Meeting, Paris, France, November 18-19, 1999

[15] O. Braillard, S. Guieu, J. Hosler, G. Sliter « Tests of Passive Autocatalytic Recombiners for Combustible Gas Control in Nuclear Power Plants », 2nd Meeting on ARS, Orlando, Florida, June 1-5, 1997

[16] J. Snoeck, C. Solaro, P. Moeyeart « First Experience with the Installation of PARs », Workshop on the Implementation of Hydrogen Mitigation Techniques, Winnipeg, Canada, May 13-15, 1996

[17] J. Rohde, W. Klein-Heßling, A.K. Chakraborty « Development and Validation of a Catalytic Recombiner Model for the Containment Code RALOC MOD 4.0 », Workshop on the Implementation of Hydrogen Mitigation Techniques, Winnipeg, Canada, 13-15 May 1996

[18] F. Fineschi, G. Fiore « A Physical-Mathematical Model to Simulate Hydrogen Passive Catalytic Recombiners », International Post-SMiRT Seminar 18, Pisa, Italy, August 25-27, 1997

[19]   G. Avakian, O. Braillard « Theoretical Model of Hydrogen Recombiner for a Nuclear Power Plant », 7th International Conference on Nuclear Engineering, Tokyo, Japan, April 19-23, 1999

[20]   M. Tahara, H. Oikawa, K. Arai « A 3-Dimensional Fluid Dynamic Analysis for a Passive Catalytic Recombiner », 7th International Conference on Nuclear Engineering, Tokyo, Japan, April 19-23, 1999

[21]   M. Heitsch « A Two-dimensional Model of Internal Catalytic Recombiner Behavior », 6th International Conference on Nuclear Engineering, San Diego, United States of America, May 10-14, 1998

[22]   P. Royl, H. Rochholz, W. Breitung, J.R. Travis, G. Necker, A. Veser « GASFLOW-Analysen zur Wirksamkeit eines Rekombinatorkonzepts bei einem postulierten Surge-line LOCA im Kernkraftwerk Neckarwestheim-2 », Wissenschaftliche Berichte FZKA 6333, März 2000

[23]   H. Hosler, G. Sliter « PARs for Combustible Gas Control in ALWR », Workshop on the Implementation of Hydrogen Mitigation Techniques, Winnipeg, Canada, May 13-15, 1996

[24]   EUCOFA – Concerted Action on Future Experimental Containment Facilities in the European Union CUNT-EUCOFA (98) P004, July 1998