Abstract. Hydrogen recombiners, recently introduced in the French nuclear reactor buildings, display high temperature (up to ca. 900°C) and several thousands square meters of a very reactive surface when operating during a severe accident scenario. Small scale analytical experiments show that cesium and cadmium iodides are unstable, and generate volatile iodine, when heated in an oven that reproduces most physico-chemical parameters of recombiner operation. Based on these results, and due to its potential with regard to the environmental source term of a severe accident, iodine chemistry in hydrogen recombiners deserves close and careful scrutiny.

1. INTRODUCTION

Hydrogen release by fuel cladding oxidation during the early stage of a postulated severe accident in a Nuclear Power Plant (NPP) can lead to potentially explosive mixtures in the air-filled containment building. Therefore, Passive Autocatalytic Recombiners (PARs) are currently implemented in the French PWR, following a decision of the French Nuclear Safety Authority. PARs are also incorporated into the design of the European Pressurized water Reactor (EPR) and considered, together with the ex-vessel core-catcher, as an important safety improvement.

Hydrogen recombiners are indeed at the centre of hydrogen mitigation strategies. They aim to "recombine" hydrogen and oxygen through the exothermic reaction $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ on an alumina-supported Pt (and Pd) catalyst, generally set up in a row of equally spaced vertical plates (with hundreds of plates in a single recombiner unit). The heat generated by the reaction powers the gas flow through the device, hence the term "passive", meaning without external power or operator action. Numerous experiments have consistently concluded to the efficiency of commercially available hydrogen recombiners, even in potentially poisonous atmospheres or under aspersion. Hydrogen recombiners (ca. 40 units per reactor building) fulfil the stringent requirements for a system implemented in a nuclear containment.

More specifically, possible side effects, and unwelcome consequences, have been also investigated, which focused onto the ignition potential of recombiners under transient overloads. Albeit this issue is not completely settled, it has been concluded that this unwanted characteristics — recombiners operating as igniters — would not create additional hazard. On the other hand, the chemical reactions likely to occur in the reactive and high temperature recombiner environment have been surprisingly overlooked. Yet, during recombiner operation, a mixture of gases carrying small labile particles will be heated at temperatures as high as 900 °C, for sufficient length of time to initiate or even bring to a state of completion, both homogeneous and heterogeneous chemical reactions (the latter implying contact with the catalytic surface). Considering the wealth of data pertaining to comparatively slow chemical reactions in the reactor building, on the containment walls or in the sump, the so far underrated issue of additional chemical reactions in the hydrogen recombiners deserves, without a doubt, more scrutiny.

2. BACKGROUND

Since iodine source term is the main concern in the management of a severe accident in a NPP, it is legitimate to investigate into iodine chemistry in hydrogen recombiners. Whereas iodine chemistry benefited from a considerable amount of severe accidents-related studies, both experimental and theoretical, these studies focussed on two particular thermochemical domains: high temperature reducing atmosphere (primary circuit), and low temperature oxidizing atmosphere (containment). The high temperature oxidizing atmosphere, typical of recombiner operation, was given comparatively few credit. Air ingress is prototypal of such a thermochemical environment, in which iodides deposited in the primary circuit vaporise and release gaseous iodine [4]. Hydrogen combustion in the containment is also relevant: a few studies have shown that, in certain conditions, hydrogen burn involves decomposition of cesium iodide [5].

Although there are still some uncertainties, most investigations, including in-pile experiments, point out to the fact that the largest fraction of radionuclides does not enter the containment as gas or vapours, but as aerosol particles — namely iodides in the case of iodine isotopes. In this latter case, cesium iodide is by far the main carrier of iodine at the break [6], together with minute amounts of silver, indium and cadmium iodides. As compared with thermodynamic equilibrium calculations, experimental results from PHEBUS-FP yielded a somewhat higher gaseous/total iodine ratio in the gas and aerosol mixture entering the containment [7]. However, in any case, the decomposition of even a tiny fraction of cesium iodide while crossing a recombiner in operation will have a significant impact upon the said ratio in the recombiner flue gas.

The aim of the RECI (RECombiner & Iodine) program was, precisely, to quantify this iodide → iodine conversion in realistic conditions of recombiner operation, albeit under the following constraints: the experiments were to be performed with non-radioactive substances, and without hydrogen [8].

3. The RECI PROGRAMME

Thermodynamic calculations show clearly that iodides are not chemically stable within an operating recombiner, their stability decreasing from CsI to CdI$_2$, with AgI and InI in-between. Heating these iodides up to 900°C in a mixture of air and water vapour yields volatile iodine compounds (I + I$_2$, HIO and HI) and either the metal (Ag), the oxides (In$_2$O$_3$ and CdO) or the hydroxide (CsOH). Iodide vapours (CsI + Cs$_2$I$_2$, and AgI) still coexist in the recombiner flue gas when the most stable iodides are at stake.

Due to the comparatively short residence time of the iodide particles in the recombiner, attainment of thermochemical equilibrium, which requires vaporization and homogeneous chemical reaction, might be hindered by kinetic processes. Heat transfer calculations show that micro-metric iodide particles are almost instantaneously in thermal equilibrium with the gas that transport them [9]. Hence, considering the melting point of the most refractory iodide of interest — $T_r$(CsI) = 626°C — iodide particles are liquid in most parts of the recombiner inter-plates channels. Moreover, complete vaporisation of the liquid droplets is achieved in time lengths (ca. 0.5 s, depending on the droplet diameter) of the same order of magnitude as their residence time in the recombiner [10]. On the other hand, chemical kinetics cannot be easily and reliably sorted out in a heterogeneous mixture with strong temperature and concentration gradients, in presence of catalytic material. Therefore, as a first step, it was decided to resort to a small scale analytical experiment, in a chemical reactor that mimics the key features of a recombiner in operation.
Figure 1. The RECI experimental test bench.

The experimental test bench (Fig. 1) consists basically of four units [11].

- **Aerosol generation**: an ultrasonic aerosol generator atomises the aqueous solution of a water soluble iodide. Monodispersed droplets are then dried, yielding iodide particles, the size of which is determined by the concentration of the solution. The input power of the ultrasonic acoustic transducer sets the aerosol concentration.

- **Recombiner surrogate**: a clear fused quartz or alumina tubing, which can accommodate a catalyst foil\(^2\), is heated in a vertical tube furnace (Fig. 2).

- **Aerosol characterization**: particles concentration and size distribution measurements are carried out by various and complementary methods\(^3\), after on-line sampling at the inlet or outlet of the heated tubing.

- **Gaseous iodine analysis**: three independently calibrated methods\(^4\) are implemented in the flue gas, downstream from an HEPA filter.

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2. Cut out of an industrially available recombiner plate.
3. Tapered Element Oscillating Microbalance (TEOM), Scanning Mobility Particle Sizer (SMPS) and Electrical Low Pressure Impactor (ELPI).
The aerosol generator thus selected limits the RECI programme to the study of water soluble substances, namely cesium and cadmium iodides: silver iodide is insoluble in water, and indium monoiodide is hydrolysed. However, the experimental results can be interpolated with reasonable confidence, since CsI and CdI₂ are the two end-terms in the stability range of the relevant iodides.

4. SUMMARY of RESULTS

4.1 Iodine chemistry

The RECI experimental setup allows to quantify, as a function of relevant parameters, the conversion of iodide particles into gaseous iodine when crossing the recombiner surrogate. For the two metal iodides of interest, we defined a so-called conversion yield:

\[ \tau_{\text{CsI}} = \frac{[\text{I}_2]_{\text{out}}}{[\text{CsI}]_{\text{in}}} \times \frac{M_i}{M_{\text{CsI}}} \]
\[ \tau_{\text{CdI}_2} = \frac{[\text{I}_2]_{\text{out}}}{[\text{CdI}_2]_{\text{in}}} \times \frac{2M_i}{M_{\text{CdI}_2}} \]

where concentrations are expressed as mass per unit volume.

The relevant parameters, and their range of variation, were chosen in accordance with most settings of in-pile and out-of-pile experiments, together with containment aerosol and recombiner operation modelling:

- temperature of the tube furnace (from 500°C up to 950°C),
- residence time of the aerosol in the heated section of the recombiner surrogate (from 0.15 s to 0.50 s),
- aerosol diameter from 0.3 µm to 1.0 µm (0.6 µm < AMMD⁵ < 2.3 µm).

Aerosol concentration was not considered as an independent parameter: it varied from 5 mg.m⁻³ up to 50 mg.m⁻³, depending on particles size. The possible influence of the catalytic material on the conversion yields was also investigated, allowing to compare purely thermal, and hypothetical thermocatalytic decomposition of the iodides.

As an example, results of thermocatalytic decomposition of CsI and thermal decomposition of CdI₂ in air at 800°C are presented in Fig. 3 and 4, respectively. At such a temperature, though lower than the maximum temperature of recombiner operation, gaseous iodine production is yet easily measurable. The highest conversion yields are generally observed for the smallest particles, suggesting that aerosol vaporization, and not chemical kinetics, is the limiting step in the iodide → iodine conversion. For the longest residence times investigated, and thermocatalytic decomposition, the conversion yield can come close to its thermodynamic equilibrium value. This upper theoretical limit is dependent on aerosol concentration (and thus, particles diameter) in the case of CsI, but it practically always reaches 100 % with CdI₂ — the oxide being the stable form of cadmium crossing a recombiner in operation.

⁵ Aerodynamic Mass Median Diameter.
The whole set of results from the RECI CsI or CdI$_2$ tests grid can be displayed on a single diagram, as in Fig. 5, which clearly exemplifies the highest conversion yields at the high temperature and small particles corner of the diagram. As expected, comparatively higher conversion yields were measured for cadmium iodide [12] as compared with the most stable cesium iodide [13]. Note that Fig. 3 and 4 could be misleading, since thermocatalytic decomposition of CsI is compared with thermal decomposition of CdI$_2$. The stability difference between both iodides is more conspicuous when the same decomposition process (thermal, or thermocatalytic) is at stake.
4.2 Aerosol physics

Subsidiary results of the RECI experiments are displayed in Fig. 6. Indeed, when vapours condense downstream from the recombiner surrogate, they generate ultra-fine particles that were not initially present in the aerosol feeding the heated tubing. At temperatures above 800°C (for CsI), the resulting size distribution of the aerosol in the flue gas is bimodal: in our experiments with CsI and CdI₂, this ultra-fine particles are most likely CsI and CdO, respectively.

Conversely, the initial size distribution is shifted towards slightly smaller particles, and smaller concentrations. The aerosol mass balance is not preserved, since a significant amount of iodide vapour condenses on the inner wall of the cold section of the tubing.
5. DISCUSSION

Due to the very high values of the iodide $\rightarrow$ iodine conversion yield, and before deriving these findings in terms of iodine chemistry in the containment, questioning the representativeness of the RECI experiments is a prerequisite. Features and artefacts distancing the RECI experiments from the genuine recombiner operation can be listed as follows:

- lack of hydrogen,
- low water mixing ratio (ca. 1.5 %),
- over-simplified composition of the carrier gas,
- lack of refractory aerosol.

In addition, the influence of a more severe chemical quenching than in an actual recombiner "chimney", which could hinder the reappearance of iodides at the expense of gaseous iodine, is unknown. The same uncertainty stands for iodide deposition and iodine adsorption in the cold sections of the tubing (fused quartz or alumina + PTFE).

The lack of hydrogen in the RECI experiments precludes all investigations into the possible effects of diffusiophoresis and Stephan flow on the iodide aerosol rate of decomposition. Numerical modelling indicates, however, that thermophoresis (also effective in the RECI heated tubing) is the dominant phoretic process [14]. On the other hand, hydrogen would not shift the chemical equilibria in a gas mixture where water vapour is the main constituent, but a more humid atmosphere (e.g., mixing ratio of 50 % at 85°C) would certainly tend to increase the iodide $\rightarrow$ iodine conversion yield.
Other fission products may react with volatile iodine to form non-volatile compounds. We recall here that all RECI experiments were carried out with stoechiometric cesium/iodine or cadmium/iodine ratios, instead of the more realistic Cs/I ≈ Cd/I ≈ 10. At last, it is likely that adsorption on refractory and unreactive aerosol will behave as a sink for volatile iodine in the recombiner flue gas, a process that is missing in the RECI experiments.

Since they bear antagonist effects on the iodide → iodine conversion, it is impossible to assess the overall impact of these chemical and physical departures of the RECI experiments from the actual recombiner operation. Either way, partial decomposition of metal iodide particles in a recombiner is bound to happen. Therefore, iodine chemistry in hydrogen recombiners is worthy of more research in order to quantify reliably the magnitude of volatile iodine generation during catalytic hydrogen combustion.

6. CONCLUSION

RECI is a 2½ year experimental programme that was brought to completion as of October 2004. The comprehensive tests grid allowed to investigate into the decomposition of cesium and cadmium iodides under thermal-hydraulics conditions that mimics the recombiner operation, despite the technical limitations of the RECI test bench. The instability of metal iodides, in a wet and oxidizing atmosphere, already demonstrated in chemistry laboratories, has been confirmed in more relevant physico-chemical conditions. The high conversion yields obtained do not come as a surprise since the RECI experiments provide a close analogy to the processes known as spray drying and spray (reactive-, or oxidizing-) pyrolysis, widely used in the laboratory and in the manufacturing industry (Fig. 7). Both processes capitalize upon the high surface/volume ratio of aerosol particles to master comparatively slow chemical reactions and to produce nano-particles, the precursor material being often a finely powdered metal halide [15].

Figure 7. The RECI test bench as a spray pyrolysis reactor.
The high rates of iodine generation, as obtained in the RECI experiments, ought to be confirmed by both numerical modelling and experiments, the latter at a somewhat larger scale in order to reproduce more closely the actual functioning of a recombiner. In particular, replacing the electrical furnace by catalytic plates heated through the exothermic recombination reaction will allow to get rid of the temperature as a key parameter for expressing the iodide → iodine conversion yield. Reporting this conversion yield as a function of hydrogen concentration will allow to validate much more accurately numerical codes of iodine behaviour in a containment including hydrogen recombiners. IRSN is presently investigating into both directions — experimental and modelling — in order to derive RECI results (iodine chemistry in hydrogen recombiners) into iodine chemistry in the containment and, eventually, to assess the recombiners impact on the iodine environmental source term.