

CATALYTIC MITIGATION OF HYDROGEN RISK DURING WET TRANSPORTATION OF RADIOACTIVE MATERIALS

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Abstract

Major challenges in the area of wet transportation of radioactive materials are reliability and safety of transportation casks. In most cases, the bottom part of the cask is filled with water whereas a gaseous mixture is contained in the upper part. In such a configuration, water radiolysis leads to the formation of hydrogen and oxygen, which continuously enriches the gaseous mixture. Among the functions to be satisfied, wet transportation systems shall thus allow the control of the hydrogen content below its flammability limit. This is currently achieved by limiting the transportation duration so as to reopen the cask before the critical hydrogen concentration is reached. Development of new technologies that would mitigate the hydrogen risk is all the more motivated because it would allow an extension of the transportation duration.

AREVA-TN International and the Institut de recherches sur la catalyse et l'environnement de Lyon have developed a catalytic system which aims at buffering the hydrogen concentration far below the flammability limit. The principle of this catalyst is to recombine the hydrogen with the oxygen formed by water radiolysis.

The present paper gives an overview of the development of this catalytic recombining system. It describes the laboratory tests undertaken for the evaluation of the recombining efficiency. Particular attention is placed on the recombining efficiency after immersion of the catalyst in borated water, which would occur in a nuclear reactor pool during loading of used fuel. Laboratory investigations, carried out in an autoclave simulating a transportation cask, showed that, after immersion in borated water, the catalytic system allows the recombination of 3% hydrogen in less than 24 hours at temperatures as low as 35 °C.

INTRODUCTION

Catalytic systems have already been developed for mitigating hydrogen risk in case of a severe accident in a nuclear power plant <1>. These catalysts were based on the use of a mixture of platinum and palladium deposited on alumina. This catalytic system enhances the oxidation of hydrogen and allows the recombination of about 1 μmol of hydrogen per second and per gram of catalyst at 90 °C.

As a matter of fact, the applicability of this technology to wet transportation requires the system to be acceptable at lower temperatures, down to about 50 °C. In addition, the catalytic support for the platinum and palladium elements shall withstand the humid environment of wet transportation of used fuel. Therefore, stainless steel is better adapted than alumina.

Consequently, AREVA-TN International together with the Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON) developed a catalytic system based on the deposition of

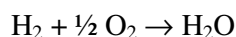
Palladium and platinum on a stainless steel grid. At first, the present paper shows the qualification results with respect to laboratory tests carried out with this recombiner. Secondly, details are given on the possible use of the recombiner for a wet transportation system.

1. QUALIFICATION OF A HYDROGEN RECOMBINER

1.1 Description of the hydrogen recombiner catalyst

The hydrogen recombiner developed by IRCELYON is composed of a combination of precious metals, i.e. platinum and palladium, deposited on an AINSI 304 stainless steel grid.

The precious metal combination is catalysing the oxidation of hydrogen with respect to the following reaction:



Therefore, the presence of oxygen within the given gaseous mixture is absolutely essential for the catalytic recombination to occur (the recombination of 1 mole of hydrogen requires half a mole of oxygen).

In order to apply these recombiners in AREVA-TN International's casks, the catalysts have to fulfil following requirements:

a) Their capacity of recombining hydrogen has to be sufficient for ensuring a hydrogen content, within the gaseous part of the cask, that remains below the flammability limit during the whole transport duration.

b) in many cases, the catalysts will be kept into water while loading the casks. This particularly occurs for loading of used fuel on a nuclear power plant site. Consequently, the catalysts have to withstand the acidity of the reactor pools as well as the presence of boron in the water. They need to keep their efficiency after dipping into borated water and their recombination capacity shall be totally regenerated at the beginning of each transport.

Qualification tests carried out at IRCELYON consisted in assessing the hydrogen recombination capacity of the catalytic system after immersion into borated water. Particular attention was placed on the influence of temperature on the recombination rate.

1.2 Preliminary recombination studies

The experimental set-up is shown in Appendix 1. It consists in an autoclave equipped with injections and analyses systems, respectively.

The preliminary tests were carried out with 540 mL of a gaseous mixture composed of laboratory air in which a specific quantity of hydrogen is injected (between 2 and 3 volume per cent).

Before each test, 4.5 cm² of catalytic grid is immersed into borated water for 1.5 h. The boric acid solution contained 2662 mg/L of boron. The catalytic sample is then hooked inside the reactor so that it remains in the gaseous mixture.

The total pressure corresponds to the amount of incondensable gases enclosed in the autoclave at ambient temperature and to the steam partial pressure, which is controlled by the temperature.

The hydrogen is injected at the beginning of the test (t=0). Following injections can also be performed. The recombination rate is deduced from the measurement of the gaseous composition using gas chromatography.

The aim of the preliminary tests was to study the influence of following parameters on the hydrogen recombination capacity:

- The temperature
- The influence of successive hydrogen injections.
- The hydrogen partial pressure
- The oxygen partial pressure

1.2.1 *Influence of temperature on the recombination rate*

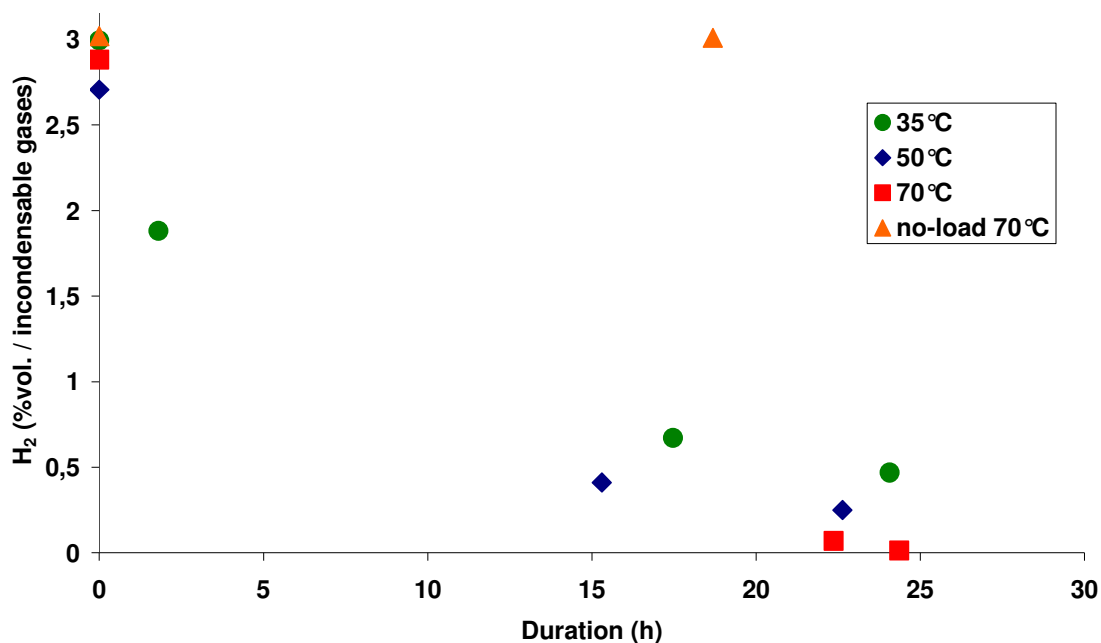


Figure 1: *Hydrogen content as a function of the testing duration for catalysts that were previously kept into borated water. Testing temperatures : 35, 50 and 70°C. The « no-load » test was performed at 70 °C without any catalyst inside the reactor.*

Figure 1 shows the evolution of the hydrogen content as a function of time for three tests performed at 35, 50 and 70 °C, respectively. The evolution of the hydrogen content can be compared with a “no-load” test at 70 °C, which was conducted without catalyst.

Following conclusions can be drawn:

- the testing reactor has no catalytic effect,
- after immersion into borated water, the recombiner is immediately active at 35 °C and at higher temperatures,
- the recombination of 3% hydrogen is possible in less than 24 hours,
- the residual hydrogen concentration is measured lower than 0.1%,
- the higher the temperature, the higher the recombination rate.

1.2.2

Influence of successive hydrogen injections on the recombination rate

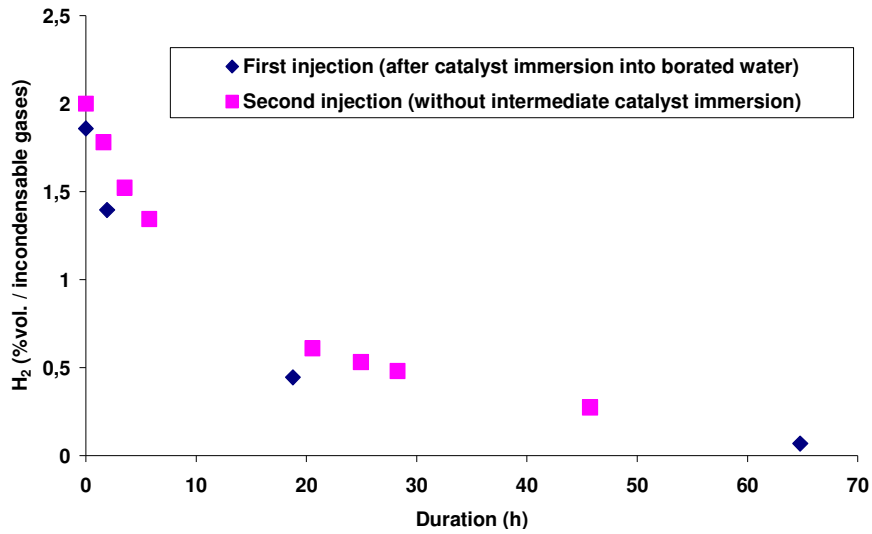


Figure 2 : *Hydrogen content as a function of the testing duration for catalysts that were previously kept into borated water. Testing temperature : 50 °C. Two successive hydrogen injections were performed without intermediate immersion of the catalytic grid into borated water.*

1.2.3

Influence of the hydrogen partial pressure

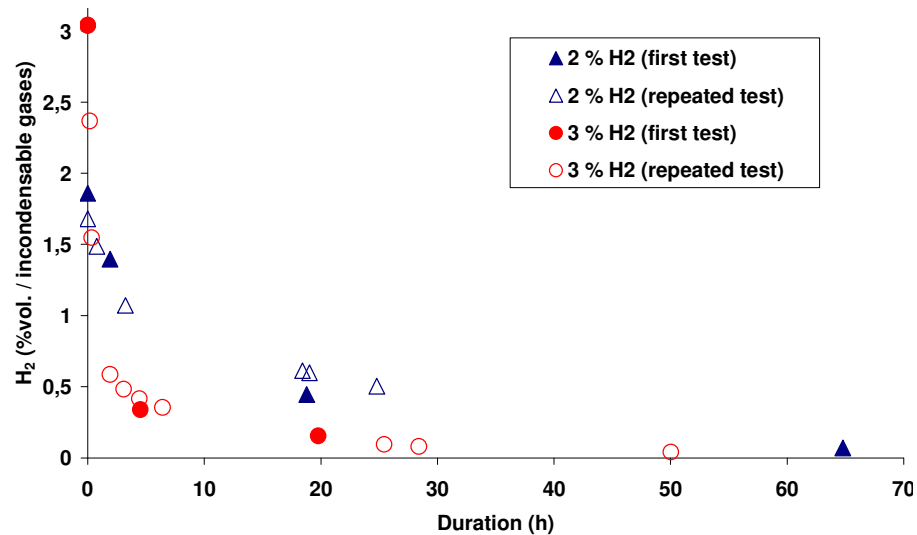


Figure 3 : *Hydrogen content as a function of the testing duration for catalysts that were previously kept into borated water. Testing temperature : 50 °C. Initial H₂ contents: 2 and 3 vol%, respectively.*

In order to study the influence of the hydrogen partial pressure on the recombination rate, two additional experiments were carried out at 50°C, in air, by injecting 2 and 3 vol% hydrogen, respectively. In addition, each experiment was repeated two times with an intermediate immersion of the catalyst into borated water.

The evolution of the hydrogen content for these two experiments is reported in figure 3.

For identical experimental conditions, the recombination rate is higher for an initial hydrogen content of 3 % H₂ as compared to that obtained with 2 % H₂ initial concentration. Indeed, one can observe a slope of the evolution curve of the H₂ concentration which shows a higher oxidation rate in case of an initial H₂ concentration of 3%. Moreover, a subsequent immersion of the catalyst into borated water followed by a subsequent repetition of the test does not show any influence on the recombination rate.

1.2.4 Influence of the oxygen partial pressure

In the following test, the air was replaced by a controlled mixture of N_2 -3% O_2 . This aimed at assessing the influence of oxygen partial pressure on the recombining capacity. At the beginning of the test, the hydrogen was directly injected into the N_2 -3% O_2 mixture.

Figure 4 shows the evolution of the hydrogen content at 40 °C in N_2 -3% O_2 , compared to the tests performed at 50, 40 and 35 °C in air.

The recombination rate at 40°C in N_2 -3% O_2 is close to the one measured in air and falls between the recombination rates at 50 °C and at 35 °C in air.

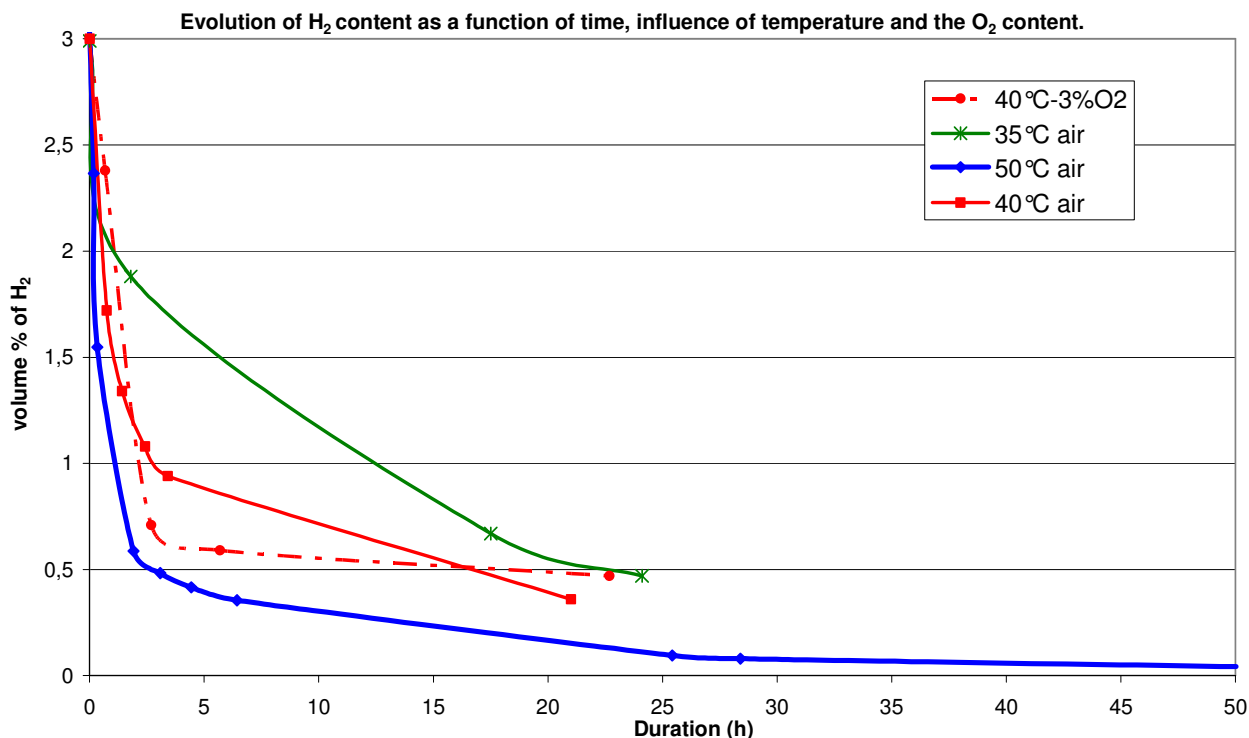


Figure 4 : Hydrogen content as a function of the testing duration for catalysts that were previously kept into borated water. Testing temperatures : 35, 40 or 50 °C. The gaseous mixture was either air or N_2 -3% O_2 .

1.3 Qualification test of the catalytic recombiner

1.3.1 Experimental protocol of the qualification campaign

Following the preliminary tests, the qualification protocol consisted in 15 immersion/recombination cycles simulating 15 loading/transport cycles. The experimental set-up was the same as previously (Appendix 1). For laboratory tests, a cycle corresponds to one week of testing defined as follows:

- 2 days immersion into borated water containing 2662 mg/l of boron.
- setting up a gaseous mixture of N_2 - O_2 containing 3 to 7 vol% oxygen.
- homogenisation of the reactor temperature at 40 °C.
- injection of 3 vol % hydrogen.
- measurement of the evolution of the hydrogen content as a function of time.
- as soon as the hydrogen content falls below 1%, an additional injection is performed in order to readjust the hydrogen concentration to 3%.
- the cycle is stopped after 5 days (1 week). The catalyst is then immersed into borated water for 2 days (week-end).

1.3.2 Qualification results.

Appendix 2 shows the evolution of the hydrogen and oxygen concentrations during the 15 immersion/recombination cycles.

The first 4 cycles were carried out with initial oxygen content of 6 to 7 vol% whereas for the last 11 cycles, this concentration was comprised between 3 and 4 vol%. It appears that this initial oxygen content has a direct influence on the amount of hydrogen injection during the corresponding cycle. With 7 vol% O₂ initially, 4 hydrogen injections are performed on a weekly basis. With 3 or 4 % O₂, only 3 injections are possible per week. Indeed, with an initial concentration of 3 to 4 % O₂, the catalytic recombination leads to a drop of the oxygen content to concentrations below 1% after about 2 days. The oxygen supply is then too small to allow the catalytic recombination with respect to the chemical reaction presented in paragraph 3.1. Consequently, for the last 11 cycles, the hydrogen content remains stable during the last few hours that follow the last hydrogen injection.

Nevertheless, appendix 2 shows that the recombination capacity remains similar for the whole 15 cycles.

1.4 Kinetics of the recombination reaction

It can be assumed that the H₂ recombination rate in cm³/h/cm² of catalytic grid can be written as follows:

$$V_{recomb} = A_0 [H_2]^\alpha \quad \text{Eq. 1}$$

where:

- V_{recomb} designates the H₂ recombination rate in cm³/h/cm² of catalytic grid,
- A₀ and α (the order of the oxidation reaction with respect to the hydrogen content) are the couple of kinetic constants for each test and
- [H₂] is the hydrogen concentration in volume %.

Based on the measured evolution of hydrogen concentration in the course of time (Appendix 2), the recombination rate was calculated for each of the 15 qualification tests performed in N₂-4%O₂ at 40°C. Figure 5 illustrates these recombination rates V_{recomb} for the two tests, which show the slowest recombination reaction. With respect to Figure 5, a conservative kinetic law for hydrogen recombination can be written as follows:

$$V_{recomb} = 0.014[H_2]^{1.5} \quad \text{Eq. 2}$$

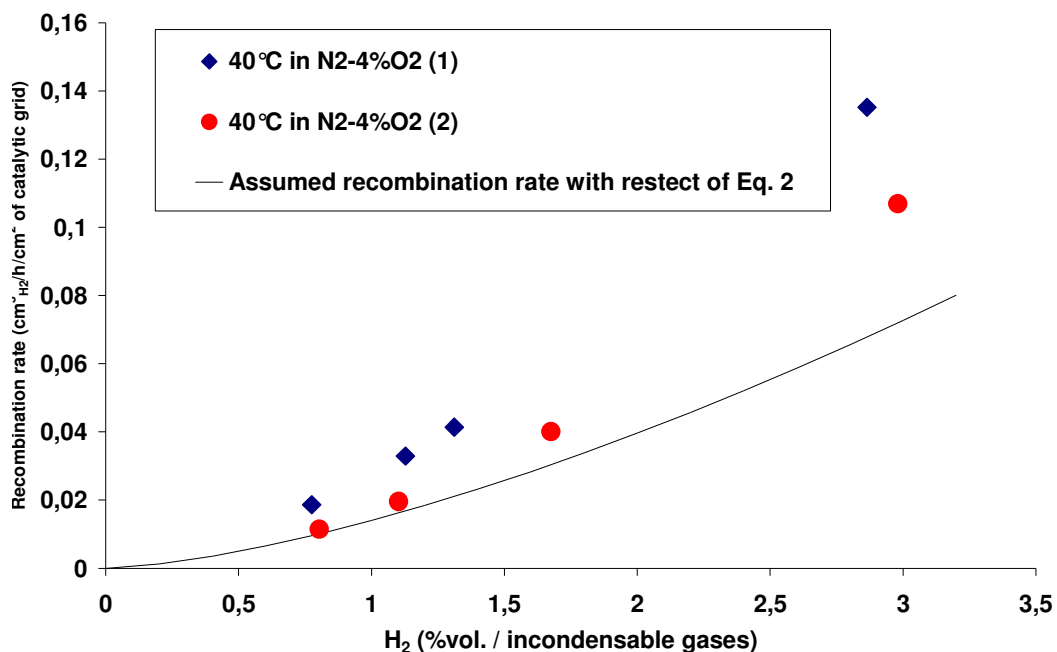


Figure 5: Evolution of the H₂ recombination rate per unit surface of the catalytic grid (in cm³/h/cm²) as a function of the H₂ concentration in the reactor at 40 °C.

For design calculations the kinetic law Eq. 2 of an order of 1.5 with respect to the hydrogen content will be considered for the oxidation of hydrogen.

2. APPLICABILITY TO THE TRANSPORTATION OF USED FUEL

Hydrogen generation due to radiolysis is usually given by a linear expression of the volume V_{prod} of hydrogen produced by unit time <2>. V_{prod} is thus given in cm^3 of H_2/h .

Consequently, in order to recombine the total quantity of hydrogen generated by radiolysis, the minimum surface S_{mini} of catalyst required is given by (in cm^2):

$$S_{\text{mini}} = \frac{V_{\text{prod}}}{V_{\text{recomb}}} = \frac{V_{\text{prod}}}{0.014[\text{H}_2]^{1.5}} \quad \text{Eq. 3}$$

As for equation Eq. 2, the hydrogen concentration in Eq. 3 is expressed in volume percentage.

An hydrogen concentration of 1% is acceptable with respect to safety since it is far below the flammability limit of 4% hydrogen in air. Therefore, it is conservative to consider that the minimum surface of catalytic grid to be put in place is given by Eq. 3 with 1 vol. % hydrogen.

As an example, R62 is a wet transportation package for used fuel presented at Patram 1986 <3>. The results of measurement of hydrogen concentrations within the package showed a hydrogen generation rate below $3.5 \text{ cm}^3/\text{h}$. This means that for the particular design of R62, a total surface of 250 cm^2 of the catalytic grid would be enough for maintaining the hydrogen concentration below 1%. It appears that such an amount of recombiner is acceptable for an application in usual transportation casks, as it should be easy to insert this low amount of catalyst within the cavity. Even higher amounts of recombiner should be easy to put in place in order to allow a safety margin with regards to recombination capacity.

Furthermore, with a higher amount of catalytic recombiner within the transportation cask, the hydrogen risk can be mitigated for a higher level of water radiolysis, i.e. for larger casks or for used fuels with higher radiation energies.

CONCLUSION

AREVA-TN International together with the Institut de recherches sur la catalyse et l'environnement de Lyon (IRCELYON) developed a catalytic system based on the deposition of palladium and platinum on a stainless steel grid. This system has shown to catalyse the oxidation of hydrogen at temperatures as low as $35 \text{ }^\circ\text{C}$, even after immersion into a boric acid water solution. The catalysing capacity has also shown to remain stable after 1400 hours of testing.

As a consequence, this system is a perfect candidate for a catalytic recombiner in AREVA-TN International's transportation casks dedicated to wet transportation. Furthermore, the recombination capacity is sufficient for stabilising the hydrogen concentration below its flammability limit, even with a low amount of recombiner. The required amount of recombiner can thus easily be introduced in a free space of the casks cavity.

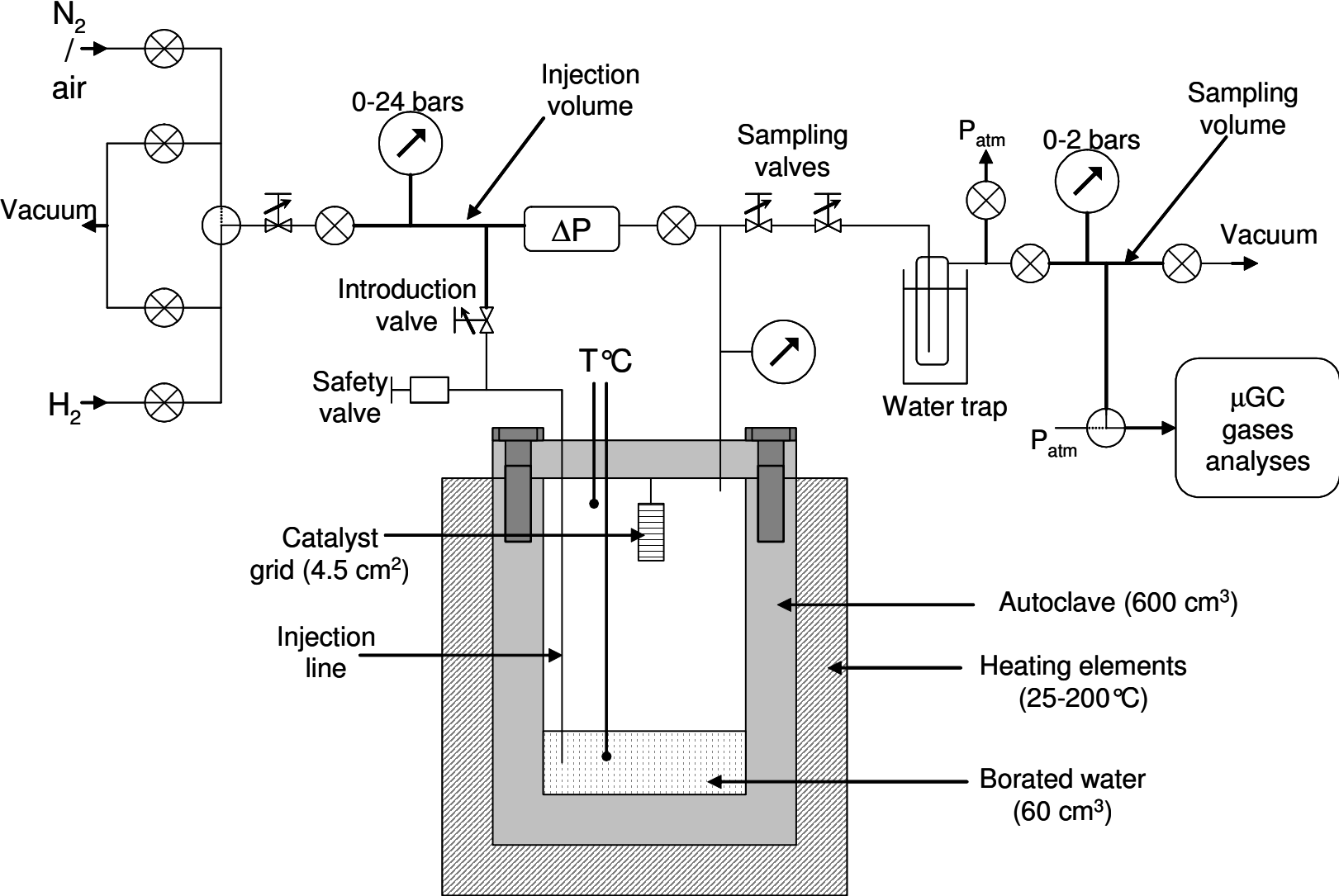
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<2>: Vinson D. W., Deible R.W., Sindelar R.L., Evaluation of hydrogen generation from radiolysis from breached used fuel, DOE document WSRC-MS-2002-000728.

<3>: Abassin J.J., Blanchard R.J., Bochart C., Campani M., Experiences paramétriques sur la radiolyse de l'eau et application à l'emballage R62 pour le transport d'assemblages combustibles défectueux, Proceedings of Patram 86 at Davos, Switzerland.

APPENDIX 1 : Experimental set-up at CNRS.



APPENDIX 2 : Qualification results.

Evolution of the oxygen and hydrogen contents during 15 immersion/recombination cycles at the laboratory

