NOVEL RELIABLE HYDROGEN RISK MITIGATION SYSTEM FOR TRANSPORTATION OF RADIOACTIVE MATERIALS

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Major issue in the area of radiolysis of radioactive materials during transportation is reliability and safety of transportation casks, especially due to hydrogen build up in the containment vessel. In the past decades, several designing options were identified to ensure that the hydrogen concentration stays below the flammability limit during the whole duration of the transport. The most common option consists in over-dimensioning the volume of the containment vessel so that it can contain all hydrogen that may be released by radiolysis of the transported material, without reaching flammable concentrations. Another option consists in using catalytic hydrogen recombiners in the casks cavity. These recombine hydrogen with the oxygen contained in the gaseous mixture. However, the working duration of these catalysts is limited by the amount of oxygen in the containment vessel.

In order to overcome this problem, AREVA TN International together with SNPE and AREVA-ELTA have developed a hydrogen risk mitigation system consisting of hydrogen recombiners, oxygen generators and oxygen release control systems that can be used for long durations to ensure a hydrogen concentration below the flammability limit.

The present paper presents this mitigation system, in particular the oxygen generator and the oxygen release control systems. Details are given on the reliability and safety assessment of this system and its conformance with the IAEA-TSR-1 regulation.

Introduction

The first designing option allowing mitigation of hydrogen risks during transportation of radiolysable radioactive materials is to overdesign the volume of the confinement vessel in order to maintain the hydrogen partial pressure below its flammability limit in all transport conditions including in the hypothesis of a total release of the hydrogen contained in the transported material, e.g. total release of the hydrogen contained in a polymeric waste or total transformation of residual water into hydrogen. This design option is still in use today and is one of the main principles used in the TN International patent <1>.

Another option consists in using hydrogen recombiners whose principle consists in recombining the hydrogen with the oxygen contained in the confinement vessel following the reaction:

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \quad (1)$$

One recent example of hydrogen recombiners has been presented at PATRAM 2007 for wet transportation of radioactive materials <2>.

The technology presented in this paper is dedicated to dry transportation of organic radioactive waste containing contaminated organic materials. Therefore the recombiners are described in TN International's patent <3> and recalled in the first section of this paper.

As a matter of fact, 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). For certain type of radioactive transports, the presence of oxygen cannot be guaranteed for the whole duration of transport.

Therefore, TN International together with SNPE and ELTA has developed an oxygen generator that can be introduced into the confinement vessel in order to release some oxygen when necessary. The solution consisting in using pressurized gaseous oxygen bottles was rejected for safety reasons. Instead, the chosen oxygen generator is a solid product totally inert in transport conditions. This generator is coupled with an electronic control system that allows the oxygen concentration in the confinement vessel at any time.

The present paper presents the hydrogen recombination system as well as the oxygen generator and their respective performances. The last part of the paper gives an overview of reliability and safety assessment of this system.

1. Hydrogen recombination system TN® Comb-A$^+$ and its performances

Radiolysis of waste containing organic polymers produces different type of gases including hydrocarbons or carbon oxides. In such conditions, the catalytic recombiner has to remain unaffected by such other gases.

For dry transportation of radioactive organic waste, TN International has developed a hydrogen recombiner named TN® Comb-A$^+$ <3>. This product allows recombination of hydrogen with oxygen in dry conditions and in presence of other type of gases released by the radiolysis of polymers. TN® Comb-A$^+$ performances have been qualified in presence of CH_4, C_2H_6, C_2H_4, CO_2, I_2, HCl and even CO gases. TN® Comb-A$^+$ has been specially developed for recombination of hydrogen in presence of carbon monoxide. Tthe latter is produced in most cases of radiolysis of polymers. On many hydrogen recombiners, carbon monoxide prevents from the hydrogen recombination. Carbon monoxide is than adsorbed on the surface of the catalyst preventing the hydrogen to react. TN® Comb-A$^+$ has been specially developed to perform both hydrogen and carbon monoxide oxidation. Carbon monoxide is thus transformed into carbon dioxide. This prevents from any poisoning effect of carbon monoxide and allows for hydrogen to be catalytically oxidized into water.

TN® Comb-A$^+$ has been qualified for temperatures up to 150 °C, which typically corresponds to the maximum temperatures during dry transportation of radioactive organic waste. It has been observed that the higher the temperature, the higher the hydrogen recombination rate

The amount of TN® Comb-A$^+$ that shall be introduced into the confinement vessel depends on two parameters: the amount of hydrogen produced during transport and the operating temperature. Following table gives, for different temperatures, the amount of TN® Comb-A$^+$ that has to be introduced into the confinement vessel to recombine 1 mole of hydrogen:

Temperature (°C)	25	45	65	›65
Amount TN® Comb-A$^+$ (in grams) needed to recombine 1 mole of H_2.	81	66	38	38

Table 1: Amount of TN® Comb-A$^+$ needed to recombine 1 mole of H_2 in presence of carbon monoxide

In addition, for TN® Comb-A+ to ensure hydrogen recombination the amount of oxygen shall be enough to allow reaction (1) before hydrogen concentration reaches the flammability limit, ie 4% hydrogen in ambient air.
As an example, the following will consider a cask containing 3 m^3 of gas. If the transport cask is loaded with air containing 20% of oxygen and the duration of transport is 1 year as required by IAEA-TSR-1 regulation <4>, the maximum hydrogen generation rate that can be recombined per reaction (1) is 3.2 L/day, i.e. 0.12 mol hydrogen per day considering ambient conditions of temperature and pressure and considering that all the oxygen is available for recombination.

For higher hydrogen generation rates it is necessary to use another source of oxygen. As an example, the subsequent section of this paper will consider a transport with a production of 2.14 mol/day of hydrogen and 0.19 mol/day of carbon monoxide. The oxygen demand for recombination is thus 1.165 mol/day. The oxygen contained in 3 m^3 of air corresponds to 600 L, which are thus totally consumed in 24 days.

2. Oxygen generator and control systems

600 L oxygen generator has been developed by SNPE. Originally developed for military and aeronautic applications <5>, this type of oxygen generator is composed of solid chlorate. Placed inside the cask cavity, the oxygen generator releases 600L of oxygen at a time when electrically activated.
The behavior of the generator has been validated for conditions representative of a radioactive transport. It has been shown that such a generator is a very safe solution Qualification tests included vibration, choc resistance, temperature resistance from -40°C to 135°C and pressure resistance at 10 mbar. It has also been demonstrated that the oxygen generator does not release the oxygen in accidental conditions of transport, ie there is no pressure increase due to an accumulation of oxygen during an accident.
Figure 1 shows the SNPE oxygen generator which corresponds to a cylinder of 135 mm in diameter and 250 mm in length.

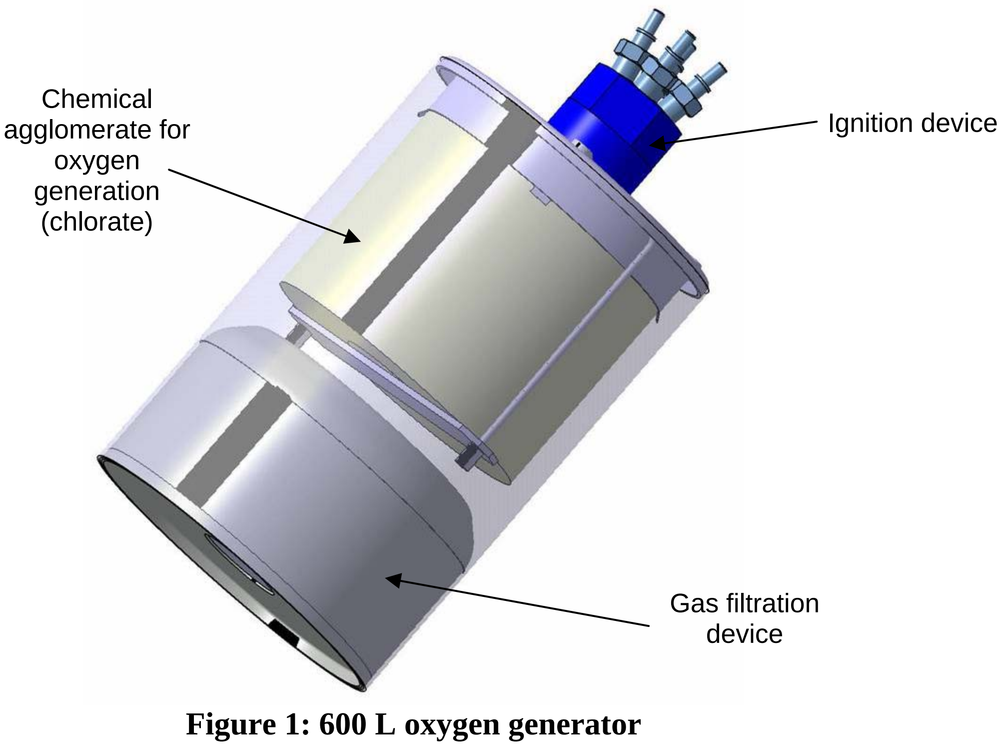

Figure 1: 600 L oxygen generator

For the example mentioned above (2.14 mol/day of hydrogen production in a 3 m^3 vessel), a minimum of 17 generators are considered to cover 1 year of oxygen demand. These 17 generators are monitored by an electronic sequencer coupled to an oxygen detector. In fact, 17 generators with 600 L oxygen each correspond to 408 days of oxygen demand. This provides an additional safety margin compared to the amount of oxygen required to recombine the maximum amount of hydrogen generated by radiolysis. Figure 2 gives details of the whole hydrogen mitigation system:

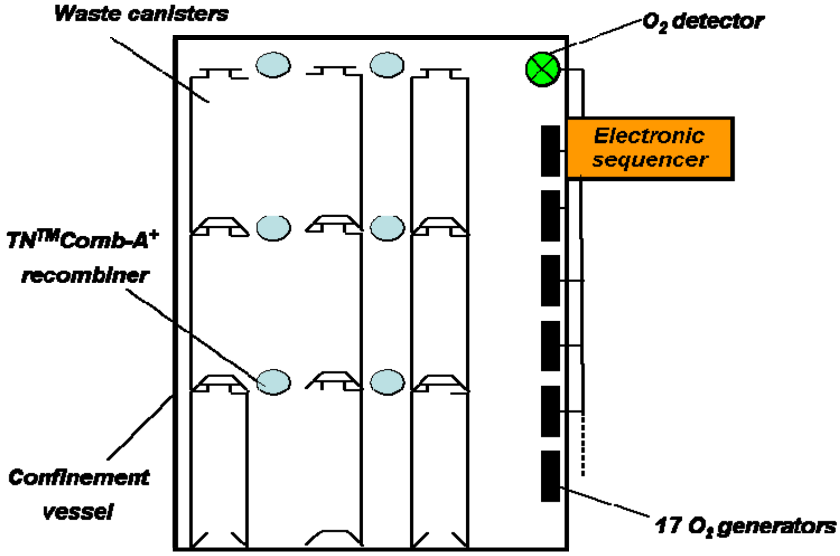

Figure 2: General view of the hydrogen mitigation system

The system comprises an oxygen detector, an electronic sequencer and a minimum of 17 oxygen generators. The following describes the minimum components required for the hydrogen mitigation system and their functions. Redundancies and friability considerations are presented in section 3.

Oxygen detector :

The oxygen detector is placed into the confinement vessel and allows for detecting the minimum oxygen concentration below which oxygen generation is required. This minimum oxygen concentration is fixed at 5%. The latter corresponds to the minimum oxygen required to cover the oxygen demand of the 7 post accidental days recommended by IAEA-TSR-1 <4> regulation. Indeed, even if there is no oxygen generation during accidental conditions of transport, the cask contains enough oxygen to recombine the hydrogen produced during 7 days. As a consequence, if an accident occurs while the oxygen concentration gets close to 5%, there is still enough oxygen for 7 days, meaning the oxygen generation system is not needed during post-accidental conditions of transport. After that, special opening procedures may be necessary.

Electronic sequencer:

The sequencer is an electronic system that links the detector to the oxygen generators. Its function is to sequence the signal received by the detector and pilot the oxygen generation in function of time. Only one generator is initiated for each signal received by the detector.

Nevertheless, within the 24 h following the initiation of a generator, the sequencer will prevent all other generator initiation even if the detector gives a signal below 5% O_2. This function gives time for the oxygen to homogenize in the confinement vessel and avoid the quasi-simultaneous initiation of all generators. Indeed, in case the gaseous mixture is not homogeneous, there is a risk for the detector to initiate several oxygen generators in very limited time period.

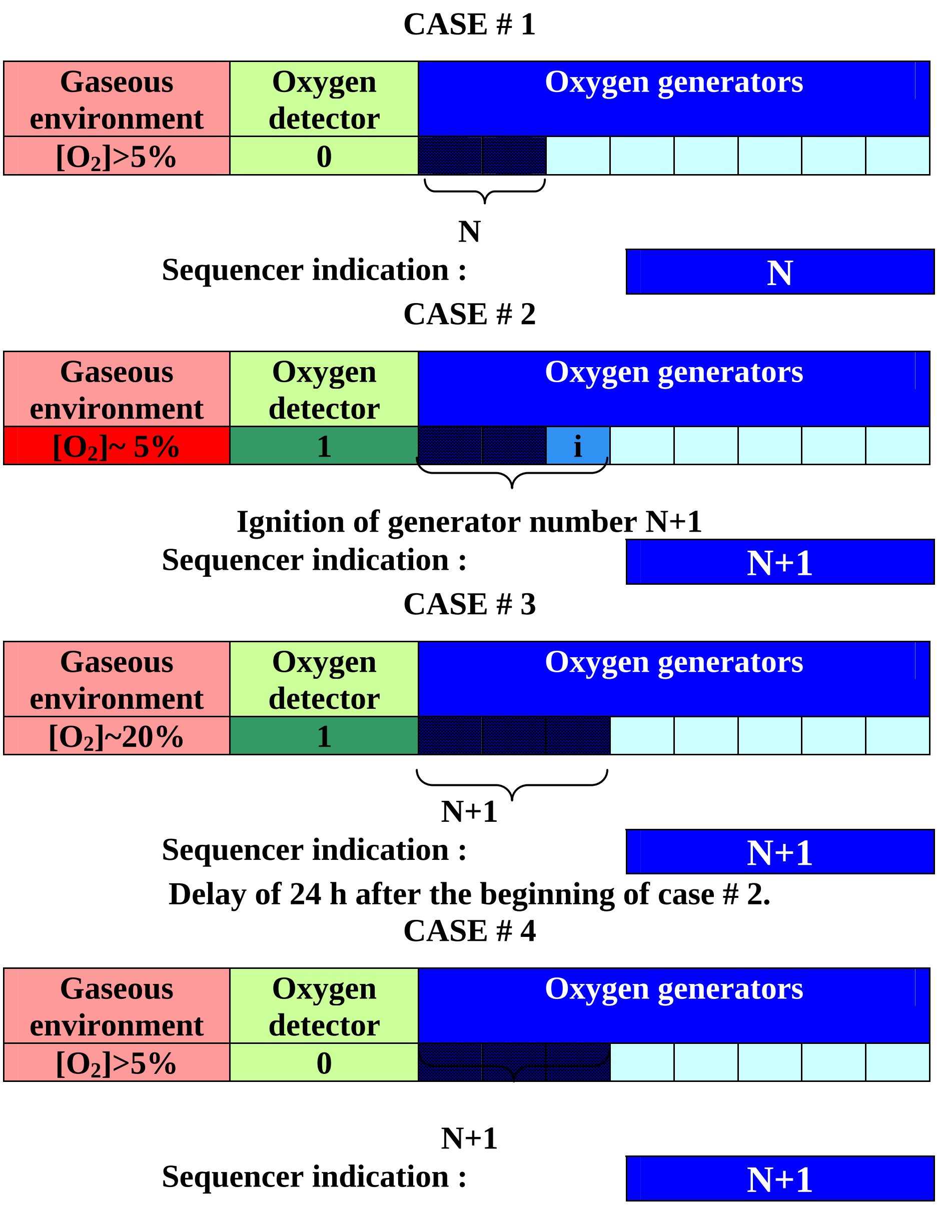

Figure 3 : 4 cases distinguished by the sequencer

The sequencer allows distinguishing 4 cases of the system made of {the gaseous environment, the oxygen detector, the oxygen generators}. These 4 cases are described below and illustrated in figure 3.

Case # 1 :
The oxygen concentration is above the 5%. The detector is in state 0. N oxygen generators have been consumed. The sequencer indicates N.

Case # 2 :
The oxygen generator is 5%. The detector is in state 1. The sequencer thus initiates the generator number N+1 and indicates N+1.

Case # 3 :
The oxygen generator number N+1 was consumed in the last 24 h. The oxygen concentration is thus above 5%. However, the sequencer prevents blocs the signal coming from the detector. The detector stays in state 1 for 24 h after the start of case # 2. The sequencer indicates N+1.

Case # 4 (similar to case # 1):
The 24 h delay is over. The oxygen concentration is above 5%. The detector is in state 0. N+1 generators were consumed. The sequencer indicates N+1.

3. Reliability and safety of the hydrogen mitigation system

Nowadays, many industries rely on electronic systems to control their processes even when a high risk is involved. For instance, airplanes are equipped with electronic systems that control engine power or wings orientation, trains are equipped with electronic systems to control braking power. In the nuclear industry, electronic systems are used for remote controls in nuclear power plants. These industries have developed probability risk assessment methods which led to the standard IEC/EN 61508 <6>, currently used for nuclear reactors control software and electronic systems. Nuclear reactors answer to the highest security integrity level, i.e. SIL4. That means it is guaranteed for a probability of dangerous failure per hour of less than 10^{-8}/h or average probability of dangerous failure less than 10^{-4}.

The same approach has been applied to the hydrogen mitigation system using the HAZard and OPerability assessment method (HAZOP) <7>. In the current mitigation system, failure is considered to occur if the confinement vessel contains either too much hydrogen or too much oxygen (i.e. simultaneous initiation of several oxygen generators). To be compliant with SIL4, these two failures are thus only allowed with a probability of 10^{-8}/h or 8,76 10^{-5}/year.

Table 2 gives the failure probabilities that were considered in the HAZOP analysis.

Component	Failure rate	Source for failure rate
Oxygen detector	5 x 10^{-6} failures/h (5000 FITS)	SINTEF database
Electronic sequencer	6,66 x 10^{-6} failures/h (6660 FITS)	Calculated by Elta
Oxygen generator	3,78 x 10^{-3} failures per generator initiation	Calculated by SNPE

Table2: Failure probability of each component of the hydrogen mitigation system

The failure probabilities for oxygen detector has been taken from the SINTEF database <8> whereas the electronic sequencer and the oxygen generator failure rates were evaluated by specific hazard and operationability assessments dedicated to these components, which would be too long to detail here. The oxygen detector and the sequencer are electronic components for which the failure can be easily expressed as a function of time whereas the oxygen detector's mission is to generate oxygen on demand as soon as it is initiated. Thus the failure rate is expressed in failures per initiation. For the purpose of the HAZOP analysis, a failure rate of 3,78 x 10^{-3} was considered. More recent data from SNPE shows that the failure rate for the oxygen generator is 3,11 x 10^{-3}. The present analysis is thus penalizing.
As a matter of fact, the components themselves do not reach the SIL4 safety level of less than 10^{-8} failures per hour. Consequently, there has to be some safety and availibity redundancies or sufficient redundancy of oxygen generators in the system architecture.

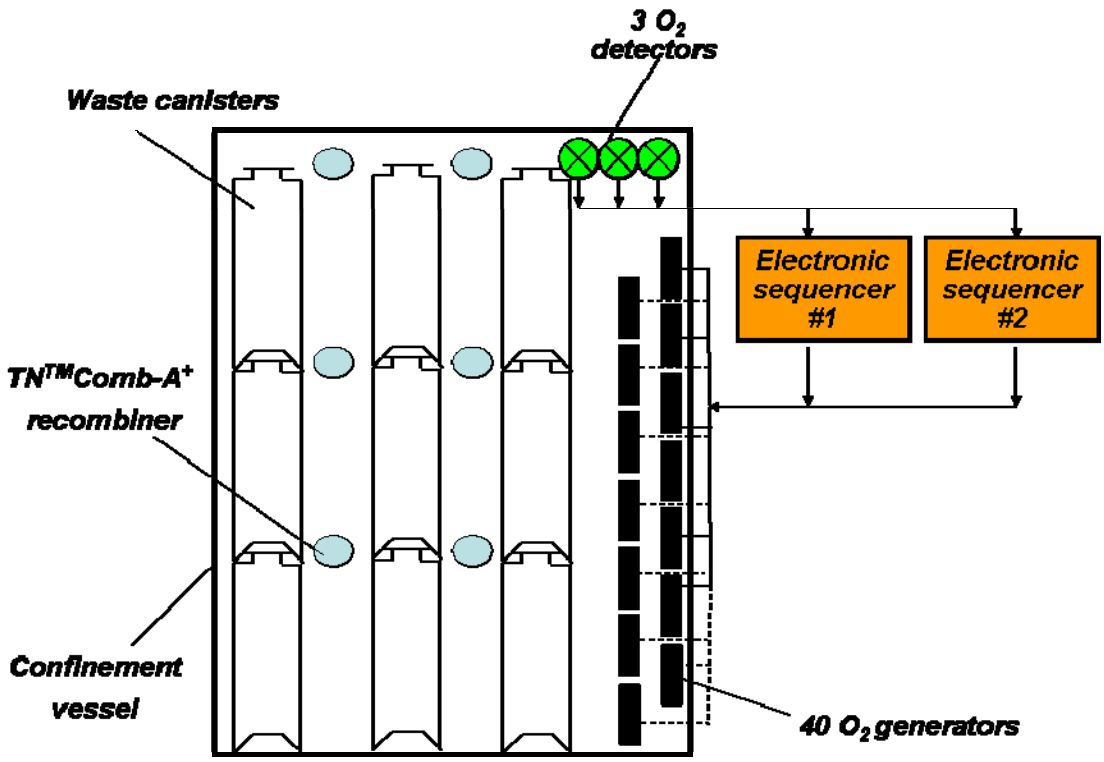

Figure 4: Schematic view of the hydrogen mitigation system with redundancy

The HAZOP method was applied to several system architectures. The following addresses the safest architecture that was analyzed. In order to reach the SIL4 level, some elements have to be redundant. Hence, the considered architecture consists in using 2 electronic sequencers in parallel, 40 oxygen generators and 3 oxygen detectors as shown in Figure 4. The 3 oxygen detectors are considered in 2oo3 redundancy (2 out of 3 voter) meaning, in normal conditions, 2 detectors out of 3 have to be in mode 1 (oxygen below 5%) according to Figure 3 for the sequencers to start a generator. Accordingly, if 1 detector is failing and is in mode 1 (oxygen below 5%), then the redundancy becomes 1oo2 (1 out of 2 voter), i.e. as soon as a non failing detector indicates an oxygen concentration below 1, the generator is initiated. The 3 detectors working in parallel with a failure probability of 5×10^{-6} each (table 2), the final failure probability reaches the SIL4 requirement if the detectors are periodically checked.

The same applies for the 2 electronic sequencers which are in redundancy 2oo2 (2 out of 2 voter), meaning that a generator is initiated only when both sequencers deliver simultaneously the initiation current to the generator. If one sequencer fails and constantly delivers initiation currents then the redundancy becomes 1oo1 (1 out of 1 voter), meaning a generator is initiated every time the remaining sequencer is delivering the initiation current.

The oxygen generators have a failure probability that can only be defined per initiation. As a consequence, the only way to reach the SIL4 safety level for the oxygen generation function is to increase the amount of generators. The proposed architecture considers 40 generators although only 17 generators are needed. The HAZOP method allowed determining the probability of not initiating at least 17 generators out of the 40. Figure 5 shows the probability of not generating enough oxygen as a function of time, i.e. the probability of accumulating hydrogen. Even at the end of one year of transport, this probability reaches 6×10^{-8}, which is still 3 orders of magnitude below the SIL4 requirement.

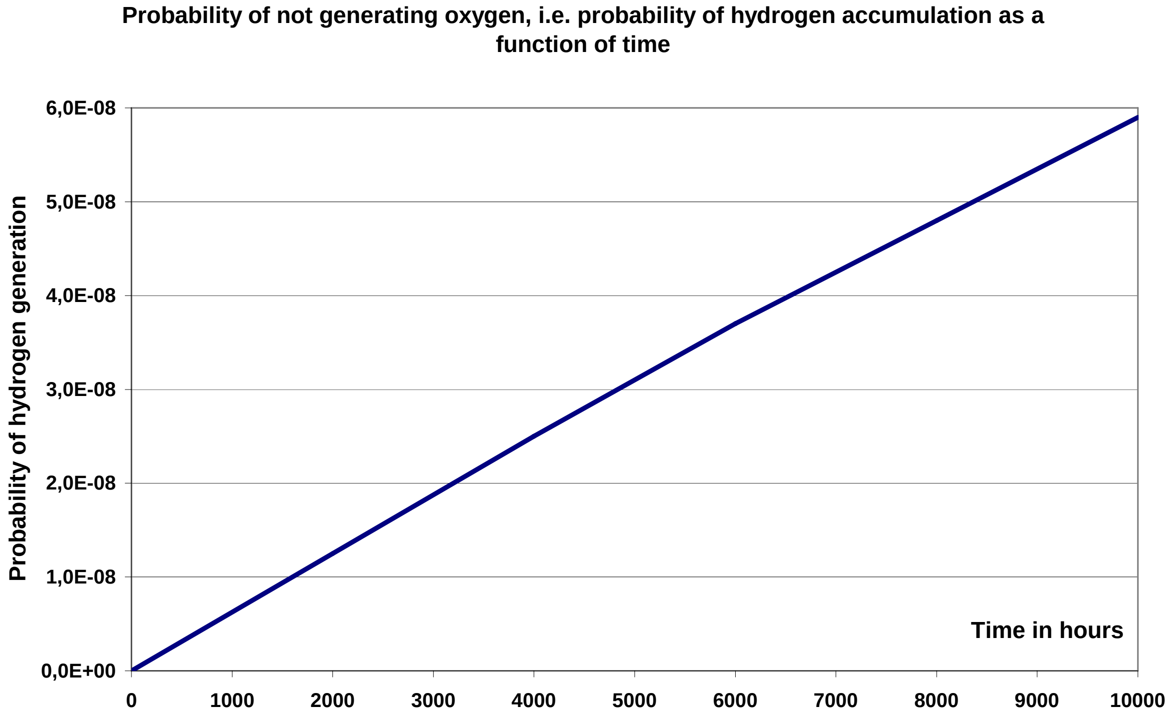

Figure 5: Probability of not generating enough oxygen or probability of accumulating hydrogen as a function of time for a 1 year transport.

Conclusion

During the last decades major innovations have relied on probabilistic safety assessment so that these types of methods are widely applied in transportation industries, such as railway metro and airplanes. Nowadays, the latter transports more than 2 billion passengers per year with airplanes equipped with electronic systems whose safety was demonstrated using probabilistic methods described in IEC/EN 61508 standard <6>. So far probabilistic safety assessments are not common in the industry of transport of radioactive materials although they are mentioned in several parts of IAEA TSG 1-1 <9> and have been applied in the past <10, 11>. The authors believe if probabilistic risk assessment were more commonly accepted in the area of transportation of radioactive materials, innovation would be enhanced and it would open large perspectives for risk mitigation and safety improvement.

The present paper presents an innovative hydrogen mitigation system dedicated to transportation with large amounts of hydrogen production by radiolysis. This patented system <12> uses a hydrogen recombiner and an electronic system that pilots the amount of oxygen available at all time. It has been shown that with this system, the probability of accumulating hydrogen is below the SIL4 safety integrity level required by IEC/EN 61508 <6> standard which is widely applied by other industries.

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