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The assessment of inherent safety and escalation hazard in the early stage design of hydrogen storage plants

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It is well known that in early design the process hazards, as well as the hazards associated to lay-out issues, may be effectively reduced by proper design solutions. In this stage of process design, a simplified and straightforward approach to the quantitative assessment of inherent safety and escalation hazard may be a suitable tool to provide guidelines for proper design choices. In the present study a specific methodology was developed for the comparison among different process alternatives under the inherent safety point of view, focusing on escalation hazard analysis. The methodology allows the calculation of key performance indicators (KPIs), quantifying both potential and inherent hazards, also related to escalation hazard, and addressing the identification of the less hazardous among possible process alternatives. In order to test the methodology, some case studies were defined, focusing on hydrogen storage technologies. The commercial and available process schemes were compared with innovative ones. Critical elements and safety distances necessary to prevent escalation effects were identified.

1. Introduction

In the framework of the expected increase of hydrogen utilisation as energy carrier storage capacities will be increased (Conte, Prosini et al, 2004; Zhou, 2005), requiring a thorough examination of the safety issues (Cadwallader and Herring, 1999). This is mostly due to the physical and chemical properties of hydrogen, which require severe operating conditions: high pressures for pressurized storages (tens of MPa), very low temperatures for liquefied storages (only tens of Kelvin) (Conte, Prosini et al, 2004; Zhou, 2005). Moreover the flammability limits are wider and the ignition energy is much lower than that of other flammable substances (Cadwallader and Herring, 1999). Thus, besides the conventional storage processes as a pressurized gas or as a cryogenic liquid, several innovative technologies were proposed, as the adsorption on metals or the storage as a complex hydride (Aiello, Mattews et al, 1999; Conte, Prosini et al, 2004; Hagstrom, Lund et al, 1995; Takeichi, Senoh et al, 2003; Zhou, 2005). However, since these technologies are at early stages of development, a large effort will be needed for their improvement. Thus a preliminary analysis and a comparison of their expected safety performances seems of fundamental importance.

The present study was dedicated to develop a set of key performance indicators (KPIs) aimed to the comparative analysis of reference technologies proposed for hydrogen storage, based on inherent safety and on escalation hazard analysis.
Since these technologies are at different stages of process development, the selection of an inherent safety assessment based on KPIs seemed a suitable approach to allow a comparative analysis. Reference process schemes for different scale hydrogen storage systems were defined for each of the alternative technologies considered.

2. Alternative technologies for hydrogen storage

2.1 Definition of different technologies proposed for hydrogen storage

In the present study, four alternative media proposed for hydrogen storage were considered: i) storage of hydrogen gas under pressure; ii) storage of liquefied hydrogen; iii) storage as a metal hydride; iv) storage as a complex hydride. These were indicated in the literature as the more effective and competitive technologies for the future development of hydrogen storage processes (Aiello, Mattews et al, 1999; Conte, Prosini et al, 2004; Hagstrom, Lund et al, 1995; Takeichi, Senoh et al, 2003; Zhou, 2005). In particular, technologies based on compressed gas and liquefied cryogenic storage are currently used worldwide for large scale applications, such as refineries or chemical plants (Conte, Prosini et al, 2004; Zhou, 2005). On the other hand, technologies based on metal and complex hydrides are still under development but are indicated as possible safer alternatives (Aiello, Mattews et al, 1999; Hagstrom, Lund et al, 1995; Takeichi, Senoh et al, 2003).
For the sake of comparison, in the analysis of the expected safety performances three different potentialities were considered for hydrogen industrial storage processes: "small", "medium" and "large" scale applications. These were defined on the basis of the analysis of technical literature and of available commercial datasheets. Details are reported in Table 1.

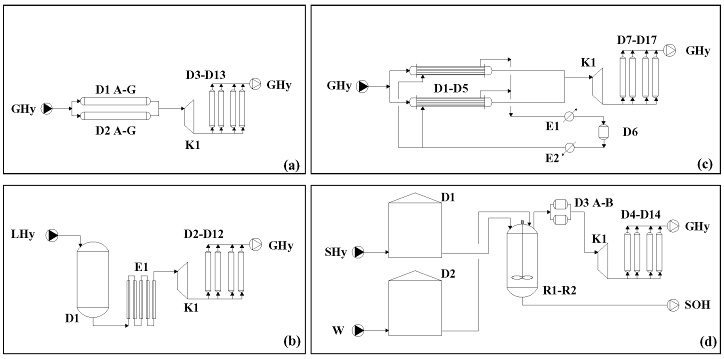
Table 1 – Definition Scale of Hydrogen Storage Systems

	Quantity (kg)	**Field of application**	**Input**	**Output**
Small Scale	5	Automotive	Gas or liquid hydrogen form refuelling	Providing gas hydrogen at 0.3 MPa to fuel cell
Medium Scale	500	Refuelling station	Hydrogen from tube trailer / road tanker	Providing gas hydrogen at 35 MPa to user
Large Scale	27000	Process / petrochemical industry	Gas hydrogen form production unit	Loading the road tanker for distribution

It is worth to recall that the aim of the present study is to carry out a comparison of the expected safety performance of the alternative storage technologies considered. Thus, other crucial issues, e.g. the actual stage of technology development, cost, storage efficiency, were not considered at this stage of the work and fall out of the scope of the present study.

2.2 Reference schemes

In order to allow a comparison among the expected safety performances of the different storage technologies considered, reference schemes were defined on the basis of literature data and of available information on existing hydrogen storage plants. Figure 1 reports the reference schemes defined for medium scale applications on the basis of the potentialities defined in Table 1.



D: storage tank
E: heat exchanger
GHy: gaseous hydrogen
K: compressor
LHy: liquid hydrogen
R: reactor/stirred vessel
SOH: exhaust hydride
SHy: hydrogen on complex hydride
W: water

Figure 1: Reference schemes for medium scale storages: (a) Compressed gas scheme; (b) Cryogenic scheme; (c) Metal hydrides scheme; (d) Complex hydrides scheme.

Techniques based on hydrogen compression (Zhou, 2005) are widely used due to their simplicity and to the lower costs of installation. Operating pressures range from 20 to 40 MPa in ordinary cases, and the gas is stored at ambient temperature. Liquefied hydrogen storage requires specific thermally insulated vessels, since temperature are very low (20-25 K). Moreover a fraction of the stored hydrogen, which is called "boil off" gas, undergoes controlled evaporation, in order to reduce heating due to the external environment heat fluxes (Zhou, 2005).

Storage on metal hydrides is based on controlled adsorption of hydrogen on metals or alloys (Hagstrom, Lund et al, 1995; Takeichi, Senoh et al, 2003), as shown in eq.(1):

$$2M + H_2 \rightarrow 2MH \qquad (1)$$

where M is a common metal. Hydrogen may thus be accumulated or released on demand by providing/removing the heat of adsorption with an adequate thermal vector, such mineral oil. Besides metal hydrides, other storage materials are under development, based on hydrolysis of particular inorganic compounds identified as the complex hydrides (Aiello, Mattews et al, 1999; Zhou, 2005). Complex hydrides are inorganic solids, such LiH, CaH_2, $NaBH_4$, etc. which strongly react with water to produce hydrogen following the eq. (2):

$$MH_x + xH_2O \rightarrow M(OH)_x + xH_2 \qquad (2)$$

The by-product is an exhausted hydroxide, which can be regenerated via reduction with carbon, e.g. obtained from biomass materials:

$$MOH^{(l)} + C^{(s)} \rightarrow M^{(l,g)} + CO^{(g)} + ½\,H_2^{(g)} \qquad (3)$$

The advantage of the complex hydride is that hydrogen may be easily stored in a stable solid matrix, which needs the controlled eq. (2) to release hydrogen and, thus, can be stored at ambient conditions, without any auxiliary system and utility.

3. Definition of a method for the comparison of storage technologies

The present analysis was aimed to the definition and calculation of inherent safety quantitative key performance indicators (KPIs) of each process and of the single process units. The flow diagram of the method, the necessary input and evaluated KPIs are shown in Figure 2.

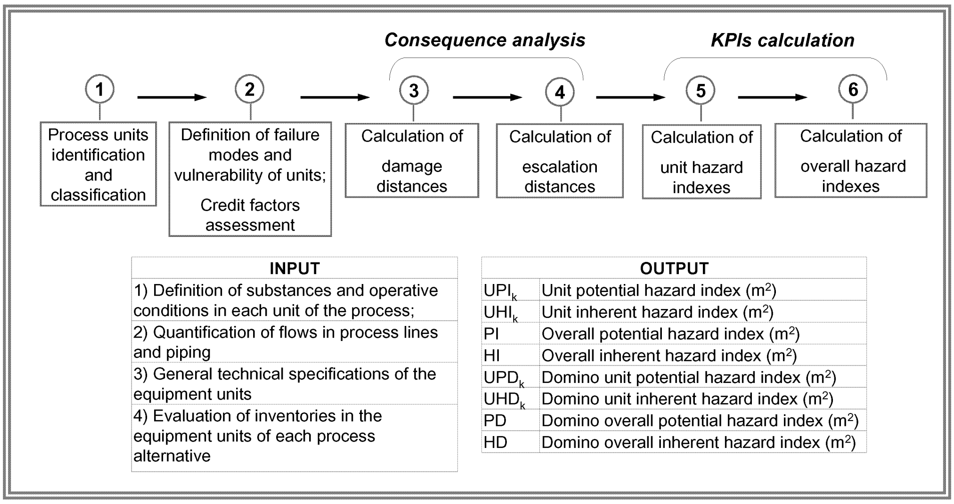


Figure 2: Flow diagram of the method.

After process units identification and classification under specific criteria, based on structural and geometrical features, different failure modes related to loss of containment (LOC) were thus associated to each unit on the basis of literature data analysis (API, 2000; Uijt de Haag and Ale, 1999). Then, a credibility factor was assessed for each LOC, on the basis of the expected release and failure frequency data reported for standard technologies in several publications (API, 2000; Delvosalle, Fievez et al, 2006; Uijt de Haag and Ale, 1999).

After the preliminary phase, the consequence analysis of each possible scenario following the identified LOC was performed. Standard event trees were used to identify the scenarios, while loss intensities and consequences were calculated by conventional literature models (Lees, 1996; Van Den Bosh, 1997) referred to several threshold values derived from technical standards and referred to damage on humans. A unit hazard vector was thus obtained, selecting the damage distance of the worst-case scenario of each LOC event considered for the unit. Further details on steps 1 to 3 of the procedure are reported elsewhere (Tugnoli, Cozzani et al, 2007).

A specific part of the methodology was dedicated to the estimation of an escalation vector for each process unit considered, aimed to the calculation of reference damage distances, following the same procedure. The escalation thresholds used were derived from previous studies (Cozzani, Gubinelli et al, 2006; Cozzani, Tugnoli et al, 2007). The escalation vector was used in the following step to provide specific domino hazard indexes.

The evaluated hazard indexes are reported in Figure 2 as an output of the method. The unit potential hazard index (UPI) was defined as the square of the maximum damage distance calculated for the unit. The UPI is thus representative of the maximum impact area that may derive from the worst case scenario considered for the unit. Following the same procedure, the unit potential domino index, UPD, was defined as the square of the maximum escalation distance calculated for the unit.

A unit inherent hazard index (UHI) was also defined, in order to consider in the analysis the safety scores of the equipment, expressed by the above defined credit factors. The UHI was calculated by the following expression:

$$UHI = \sum_{i=1}^{n} cf_i \cdot h_i^2 \qquad (4)$$

where n is the number of LOC events considered for the unit, cf_i and h_i are respectively the credit factor and the maximum damage distance calculated for the i-th LOC event of the unit. The unit domino hazard index, UHD, was defined by eq.(1), substituting damage distances, h_i, with escalation distances, e_i. The overall indexes were finally evaluated by the sum of the single unit indexes UPI and of UHI, respectevily obtaining the overall potential index (PI) and the overall hazard index (HI) of the process. These overall indexes allow the assessment of the expected overall inherent safety performance of the plant, based either on a direct assessment of potential worst-case scenarios (PI) or of likely safety performance and release scenarios of the process units (HI). The overall domino potential index, PD, and the overall domino hazard index, HD, were defined summing up respectively the UPD values and the UHD values for all the units.

4. Results

The KPIs evaluated in the present analysis are reported in Table 2. The assessment of domino escalation was not considered significant for small scale storages, which are supposed to be devoted only to automotive installations.

The table evidences that the highest potential hazard index PI was obtained for the commercial technologies, in particular compressed gas and cryogenic storage. On the contrary, innovative technologies always result in lower PI values. As a matter of fact, hydrogen is stored in a stable hydride matrix in both metal and complex hydrides schemes, which allow to reduce the potential effect of all the scenarios. Moreover, the operative conditions results less critical than the commercial schemes. Thus, also the escalation distances, in terms of the overall index PD, results limited, as reported in Table 2.

Table 2 – Overall inherent safety and escalation KPIs (in m^2)calculated for the for the four reference process schemes considered on different scales.

	KPIs	Compressed	Cryogenic	Metal hydride	Complex hydride
Small scale	PI	1.3×10^3	6.0×10^2	2.4×10^2	-
	HI	1.7×10^{-2}	1.3×10^{-1}	4.1×10^{-2}	-
Medium scale	PI	9.8×10^3	9.4×10^3	3.2×10^3	4.6×10^3
	HI	3.1×10^{-1}	5.0×10^{-1}	4.9×10^{-1}	3.3×10^{-1}
	PD	3.9×10^3	4.1×10^3	1.8×10^3	2.9×10^3
	HD	1.8×10^{-1}	3.1×10^{-1}	2.3×10^{-1}	1.9×10^{-1}
Large scale	PI	-	1.7×10^6	-	1.8×10^4
	HI	-	1.4×10^2	-	6.8×10^0
	PD	-	1.6×10^6	-	6.4×10^3
	HD	-	8.1×10^1	-	4.3×10^0

If credibility factors are introduced in the analysis, higher value of the hazard index, HI, and of the hazard escalation index HD, are obtained for the alternative technologies. This is mainly connected to the plant complexity, in terms of auxiliary equipments and secondary units. The innovative technologies, such as hydride storages, need heat transfer utilities, while the process diagram of commercial compressed storage technologies is much simpler and a more limited number of units is present. The contribution of auxiliary equipment to the overall KPIs may be important, in particular if high credibility factors are associated to LOC events from these units, such those related to the shell&tube units present in the metal hydrides scheme, both on small and medium scale. This can also be evidenced from the detailed results reported in Table 3 for medium scale storages. Moreover, the introduction of a compression unit (K1) in all the assessed schemes is crucial. The highest UHI and UHD values were associated to this unit results in all cases examined, although the damage and escalation distances are not critical.

Concerning large scale applications, the complex hydrides scheme results in low values of the KPIs (about two order of magnitude lower than those of the liquefied storage process). This is due to extremely low damage distances connected to the stability of the hydride. However, also in this case, the most critical unit resulted the compression system for both alternatives. This unit is needed in the conventional process for hydrogen liquefaction and in complex hydrides storage for hydrogen gas delivery.

Table 3 – Values of the unit KPIs (in m^2)calculated for the four alternative storage technologies considered on medium scale schemes.

Scheme	Unit	Description	UPI	UHI	UPD	UHD
Compressed	D1-D2 (A-G)	Bulk storage tanks	7.3×10^3	1.8×10^{-2}	2.3×10^3	8.7×10^{-3}
	D3-D13	Buffer storage tanks	1.4×10^3	1.9×10^{-2}	8.0×10^2	1.1×10^{-2}
	K1	Compressor	1.1×10^3	2.7×10^{-1}	7.5×10^2	1.6×10^{-1}
Cryogenic	D1	Bulk storage tank	6.8×10^3	2.0×10^{-1}	2.5×10^3	1.3×10^{-1}
	D2-D12	Buffer storage tanks	1.4×10^3	1.9×10^{-2}	8.0×10^2	1.1×10^{-2}
	E1	Vaporizer	9.4×10^1	1.5×10^{-2}	5.0×10^1	1.0×10^{-2}
	K1	Compressor	1.1×10^3	2.7×10^{-1}	7.5×10^2	1.6×10^{-1}
Metal hydrides	D1-D5	Bulk storage tanks	6.9×10^2	1.7×10^{-1}	2.0×10^2	5.0×10^{-2}
	D7	Oil buffer tank	1.1×10^1	1.8×10^{-3}	1.1×10^0	1.7×10^{-5}
	D6-D16	Buffer storage tanks	1.4×10^3	1.9×10^{-2}	8.0×10^2	1.1×10^{-2}
	E1	Heat exchanger	5.5×10^0	1.8×10^{-2}	4.5×10^0	7.8×10^{-3}
	E2	Heat exchanger	6.5×10^0	1.4×10^{-2}	5.5×10^0	5.8×10^{-3}
	K1	Compressor	1.1×10^3	2.7×10^{-1}	7.5×10^2	1.6×10^{-1}
Complex hydrides	D1	Bulk storage tank	1.5×10^3	3.5×10^{-2}	1.1×10^3	1.7×10^{-2}
	D3 (A-B)	Collector tank unit	5.5×10^1	5.0×10^{-5}	9.0×10^0	4.5×10^{-6}
	D4-D14	Buffer storage tanks	1.4×10^3	1.9×10^{-2}	8.5×10^2	1.3×10^{-2}
	R1-R2	Hydrolysis reactors	5.3×10^2	4.0×10^{-3}	4.9×10^1	4.4×10^{-4}
	K1	Compressor	1.1×10^3	2.7×10^{-1}	7.5×10^2	1.6×10^{-1}

5. Conclusions

The expected safety performance of alternative hydrogen storage technologies was explored estimating several KPIs based on consequence assessment and credibility factors of possible LOC events. Several storage sizes, related to different industrial applications, were considered. The calculated KPIs provide a preliminary screening of the expected safety performance and of the critical escalation distances for possible domino effects. The comparative analysis carried out indicated that the potential hazard is always lower for the innovative technologies proposed for hydrogen storage, mainly due to the stable behaviour of hydrides and to the less hazardous operative conditions present with respect to conventional technologies. Nevertheless, if the credibility factors of LOC events are considered, the innovative technologies show lower safety performances, mainly due to the more complex storage process, requiring a higher number of auxiliary units, and to the credibility of LOC events in standard units as compressors or shell&tube heat exchangers. Thus, the results obtained evidence that in the perspective of an industrial implementation of these technologies, the reliability of the auxiliary equipment will be an important issue to be addressed.

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