



## Inherent safety key performance indicators for hydrogen storage systems

Gabriele Landucci<sup>a</sup>, Alessandro Tugnoli<sup>b</sup>, Valerio Cozzani<sup>b,\*</sup>

<sup>a</sup> *Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali, Università di Pisa, via Diotisalvi n.2, 56126 Pisa, Italy*

<sup>b</sup> *Dipartimento di Ingegneria Chimica, Mineraria e delle Tecnologie Ambientali, Alma Mater Studiorum - Università di Bologna, via Terracini n.28, 40131 Bologna, Italy*

### ARTICLE INFO

#### Article history:

Received 7 December 2007

Received in revised form 18 February 2008

Accepted 19 February 2008

Available online 29 February 2008

#### Keywords:

Inherent safety

Major accident hazard

Safety assessment

Hydrogen storage technologies

Hydrogen storage safety

### ABSTRACT

The expected inherent safety performance of hydrogen storage technologies was investigated. Reference schemes were defined for alternative processes proposed for hydrogen storage, and several storage potentialities were considered. The expected safety performance of alternative process technologies was explored estimating key performance indicators based on consequence assessment and credit factors of possible loss of containment events. The results indicated that the potential hazard is always lower for the innovative technologies proposed for hydrogen storage, as metal or complex hydrides. This derived mainly from the application of the inherent safety principles of “substitution” and “moderation”, since in these processes hydrogen is stored as a less hazardous hydride. However, the results also evidenced that in the perspective of an industrial implementation of these technologies, the reliability of the auxiliary equipment will be a critical issue to be addressed.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

A significant increase in the use of hydrogen as an energy vector and in advanced refining technologies is expected in the next years [1–4]. The increase in the number and in the potentialities of hydrogen production plants will require a strong increase of hydrogen storage capacities [2,4,5]. Moreover, it is expected that use of hydrogen as an energy carrier may cause a spread of hydrogen storage installations also in vulnerable contexts, such as residential and commercial areas. In this framework, the further development of hydrogen storage technologies requires a thorough examination of the safety issues [6,7].

Hydrogen storage represents a well-known and widely investigated technological problem. Due to the physical and chemical properties of this substance, conventional storage processes have to manage critical operating conditions: high pressures are required by pressurized storages (tens of MPa), while liquefied storage needs lower temperatures than other cryogenic processes (a few tens of Kelvin) [1,2,8–10]. Moreover, the flammability limits are wider and the ignition energy is much lower than that of other flammable substances [6]. Thus, several innovative technologies were proposed for hydrogen storage. Examples are the adsorption on metals or the storage as a complex hydride [1,2,8,11]. However, due to the large effort still needed to develop these technologies and to the growing risk-aversion in the society, a preliminary analysis and a comparison of their expected safety performances seems of fundamental

importance. As a matter of fact, the requirement for an improved safety performance will be a key issue in the development and the diffusion of new or improved hydrogen storage technologies [12].

The present study was dedicated to develop a set of inherent safety key performance indicators (KPIs) aimed at the comparative analysis of reference technologies proposed for hydrogen storage. Since these technologies are at different stages of process development (research, pilot plant applications, industrial application), 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. The application of the developed methodology to the analysis of the reference schemes allowed the screening of the expected safety performance of alternative storage processes. The results also allowed the identification of critical safety issues that need to be addressed in the further development of inherently safer hydrogen storage technologies.

### 2. Alternative technologies proposed for hydrogen storage

Comprehensive reviews of proposed storage technologies and of related safety issues are available in the literature [1,2,4,7]. 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 [13–15], although the present stage of development of these four technolo-

\* Corresponding author. Tel.: +39 051 2090240; fax: +39 051 2090247.  
E-mail address: [valerio.cozzani@unibo.it](mailto:valerio.cozzani@unibo.it) (V. Cozzani).

**Table 1**  
Stage of development and main features of different scale hydrogen storage systems

Scheme	Features	Small scale	Medium scale	Large scale
Compressed	Technology	Commercial	Commercial	–
	Pressure (MPa)	40	25	–
	Temperature (K)	300	300	–
	H <sub>2</sub> mass stored per unit (kg)	2.5	35.7	–
	Number of units	2	2 tube trailers × 7 units	–
Cryogenic	Technology	Research	Commercial	Commercial
	Pressure (MPa)	0.6	0.6	1.7
	Temperature (K)	20/25	20/25	20/25
	H <sub>2</sub> mass stored per unit (kg)	5	500	13500
	Number of units	1	1	2
Metal hydride	Technology	Commercial	Research	–
	Pressure (MPa)	1.1	1.1	–
	Temperature (K)	300	300	–
	H <sub>2</sub> mass stored per unit (kg)	1	105	–
	Number of units	5	5	–
Complex hydride	Technology	–	Research	Research
	Pressure (MPa)	–	0.1	0.1
	Temperature (K)	–	300	300
	H <sub>2</sub> mass stored per unit (kg)	–	500	13500
	Number of units	–	1	2

gies is quite different [1,2,8,13–15]. In particular, technologies based on compressed gas and liquefied cryogenic storage is currently used worldwide for large-scale applications, such as refineries or chemical plants [13,14]. On the other hand, technologies based on metal and complex hydrides are still under development but are indicated as possible safer alternatives [13,14].

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 [1,2,8–11] and of available commercial datasheets.

“Small-scale” storages are needed in innovative automotive applications. A 5 kg storage was considered, supplying gaseous hydrogen at a fuel cell engine operating at low pressure (e.g. 0.3 MPa).

“Medium-scale” storages will be required in hydrogen refuelling stations. In several preliminary and demonstrative plants the storage unit contains about 500 kg of hydrogen. In these applications, hydrogen is supplied to the user at 35 MPa. Thus, a compression unit is also required.

Finally, “large-scale” applications are used in current industrial application, including hydrogen production and supply in oil refineries. On the basis of literature data, a bulk storage of 27 t of hydrogen was considered in the analysis. In order to have a cor-

rect overview of the hazards related to the alternative technologies, the storage facilities were considered coupled with the necessary “upstream” operations (e.g. the liquefaction unit for liquefied storage).

Table 1 reports the main features and the stage of technology development for the different scale hydrogen storage processes considered. In the case of storage based on metal or complex hydrides, some data in the table were estimated on the basis of the characteristics of the available pilot applications. More details on the technologies assessed in the present study, on the process involved and on the corresponding operative conditions are reported in Appendix A.

The purpose of the present study is to identify and compare the expected inherent safety performance of a selected set of hydrogen storage technologies. Other crucial issues for technology application (e.g. actual stage of development, cost, storage efficiency, etc.) were not considered at this stage of the work and fall out of the scope of the present study.

### 3. Inherent safety key performance indicators

The inherent safety assessment of alternative storage technologies requires the application of a methodology based on a low level of details, since some of the alternative processes considered are not yet at the stage of industrial application. Thus, inherent safety key performance indicators were defined for the quantification of the expected safety performance of each process and of the single process units.

The concept of inherent safety, introduced in the mid-1970s by Kletz [16], is now widely applied in pursuing the reduction of the hazards related to industrial processes. A well-known set of guideword was proposed to orient technology design toward inherent safety [17]. Out of them, the “substitution” guideword appears particularly appropriate to describe the difference introduced by the innovative storage technologies proposed for hydrogen storage, as hydrides. In these processes a rather hazardous substance (hydrogen) is actually replaced with a less hazardous material (the hydride) in the storage units [17]. Also the “moderation” guideword may be applied to understand the different inherent safety performance of alternative technologies, since the hydrides requires “less severe process conditions” [17]. However, the sole inherent safety principles do not yield a quantitative picture of the achieved safety

**Table 2**  
Required input for the application of the proposed method and definition of the inherent safety key performance indicators used in the present study

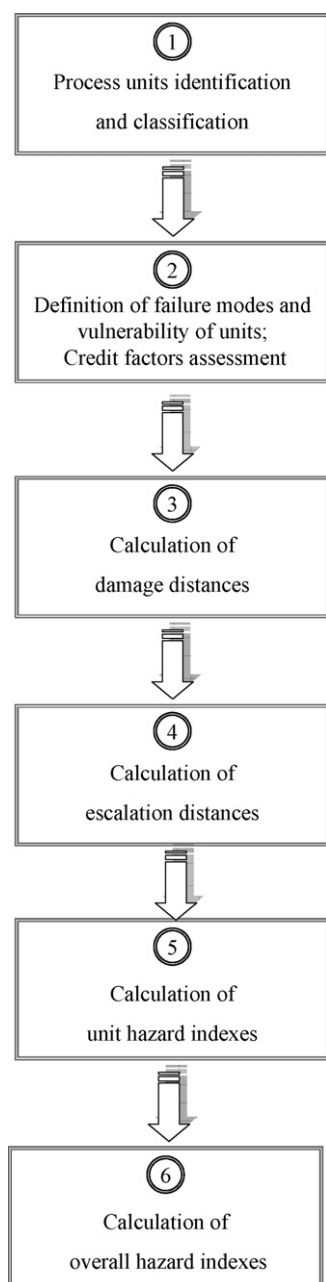
Input	
(1) Definition of substances and operative conditions in each unit of the process.	
(2) Quantification of flows in process lines and piping.	
(3) General technical specifications of the equipment units.	
(4) Evaluation of inventories in the equipment units of each process alternative.	
Output	
UPI <sub>k</sub>	Unit potential hazard index (m <sup>2</sup> )
UHI <sub>k</sub>	Unit inherent hazard index (m <sup>2</sup> )
PI	Overall potential hazard index (m <sup>2</sup> )
HI	Overall inherent hazard index (m <sup>2</sup> )
UPD <sub>k</sub>	Domino unit potential hazard index (m <sup>2</sup> )
UHD <sub>k</sub>	Domino unit inherent hazard index (m <sup>2</sup> )
PD	Domino overall potential hazard index (m <sup>2</sup> )
HD	Domino overall inherent hazard index (m <sup>2</sup> )

**Table 3**  
Threshold values assumed for the estimation of the expected damage distances

Physical effect	Threshold values	
	Effect on humans	Domino escalation
Flash Fire—transient radiation	1/2 LFL lower flammability limit, %vol	1/2 LFL lower flammability limit, %vol
Fireball—transient radiation	7 kW/m <sup>2</sup>	15 <sup>a</sup> –50 <sup>b</sup> kW/m <sup>2</sup>
Jet Fire—stationary radiation	7 kW/m <sup>2</sup>	15 <sup>a</sup> –50 <sup>b</sup> kW/m <sup>2</sup>
Pool Fire—stationary radiation	7 kW/m <sup>2</sup>	15 <sup>a</sup> –50 <sup>b</sup> kW/m <sup>2</sup>
Vapor Cloud Explosion—overpressure	0.14 bar	0.16 <sup>b</sup> –0.22 <sup>a</sup> bar
Physical/mechanical explosion—overpressure	0.14 bar	0.16 <sup>b</sup> –0.22 <sup>a</sup> bar
Toxic exposure	IDLH immediately dangerous to life and health concentration	–

<sup>a</sup> Value for atmospheric equipment.

<sup>b</sup> Value for pressurized equipment.



**Fig. 1.** Flow diagram of the method used for the calculation of the inherent safety key performance indicators.

performance. Existing methods for the evaluation of the inherent safety performance of a process are mainly aimed at the assessment of chemical reaction processes and in most cases introduce somehow arbitrary hazard indexes, derived from expert judgment [21]. Thus, literature methods for inherent safety assessment show important limits in the assessment of storage systems. To overcome these limitations, in the present approach, a specific methodology based KPIs derived from the estimation of the consequences of the potential accidents was further developed and applied to the comparative assessment of the inherent safety of process alternatives.

The flow diagram of the method is shown in Fig. 1. Table 2 reports the required inputs and the outputs provided. As shown in Fig. 1, the first step of the methodology is the identification of process units to be considered in each alternative scheme, which are classified on the basis of their structural and geometrical features. Different failure modes related to loss of containment (LOC) are thus associated to each unit on the basis of literature data analysis [18–20]. In the second step, a credit factor is assigned to each LOC, in order to assess its likelihood. The credibility of a LOC is estimated on the basis of available statistical data for failure frequencies. Equipment frequency failure data are reported in several publications. The reference values suggested for a given equipment failure mode by the “Purple Book” [18] or, if not available, by the American Petroleum Institute (API) [19] were used in the present approach as “credit factors” for standard technologies (see Appendix A for examples). The reference values reported for standard technologies by these sources may be modified to account for improved safety standards of specific pieces of equipment. In particular, a simplified Failure Mode and Effect Analysis (FMEA) was used in the present approach to obtain data for non-standard equipment.

In step 3 of the procedure, the consequence analysis of each possible scenario following the LOC was performed. Standard event trees were used to identify the scenarios, while loss intensities and consequences were calculated by conventional literature models [22,23]. The threshold values for damage to humans reported in Table 3 and derived from technical standards were used to calculate a conventional damage distance for each scenario. The conventional damage distance of the scenario was defined as the maximum distance at which the physical effects of the scenario considered equal the corresponding threshold value reported in Table 3 (see Appendix A for examples).

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 1–3 of the procedure are reported elsewhere [21].

Due to the severe potential hazard caused by escalation events in hydrogen storage systems, a specific step of the procedure (step 4 in Fig. 1) was dedicated to the estimation of an escalation vector for each process unit considered. The escalation thresholds reported in Table 3, derived from previous studies [24,25], were used to calculate the conventional escalation distances for each LOC using a

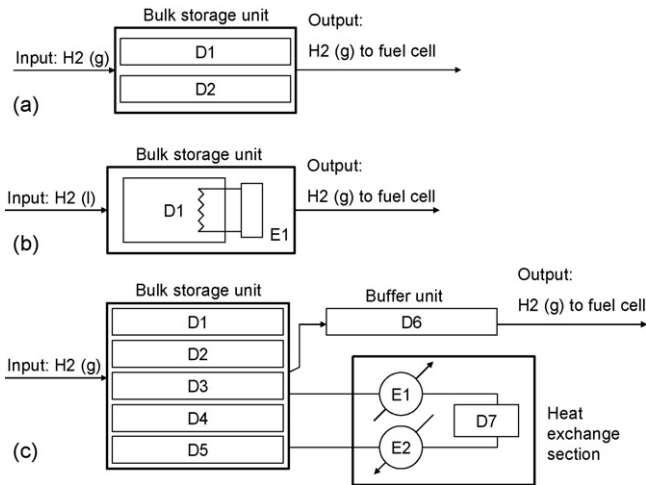


Fig. 2. Small-scale hydrogen storage processes: reference schemes considered in the analysis. (a) Compressed, (b) cryogenic and (c) metal hydrides storage technologies.

procedure similar to that applied in step 3. In particular, for each scenario following the LOC, conventional consequence assessment models were used to calculate the maximum distance at which the physical effects resulted equal to the corresponding escalation threshold reported in Table 3. The maximum distance among those calculated for all the scenarios considered was assumed as the escalation distance for the LOC (see examples in Appendix A).

An escalation vector was thus defined for each unit, the elements being the escalation distances of each LOC event considered for the unit. The escalation vector was used in the following step to provide specific domino hazard indexes.

Table 2 summarizes the inherent safety key performance indicators obtained by the procedure (steps 5 and 6 in Fig. 1). 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. A unit inherent hazard index (UHI) was also defined. The UHI was introduced 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:

$$UHI = \sum_{i=1}^n cf_i \cdot (h_i - c)^2 \quad (1)$$

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, and  $c$  is a constant. The constant  $c$ , taken equal to 5 m in the present study, was introduced to avoid considering in the analysis a number of “minor” scenarios (having a damage distance of less than 5 m in the case). This was also required by the big uncertainty of conventional consequence analysis models in the near field.

The sum of UPI and of UHI values for all the process units were used to calculate, respectively, the overall potential index (PI) and the overall hazard index (HI) of the process. These overall indexes

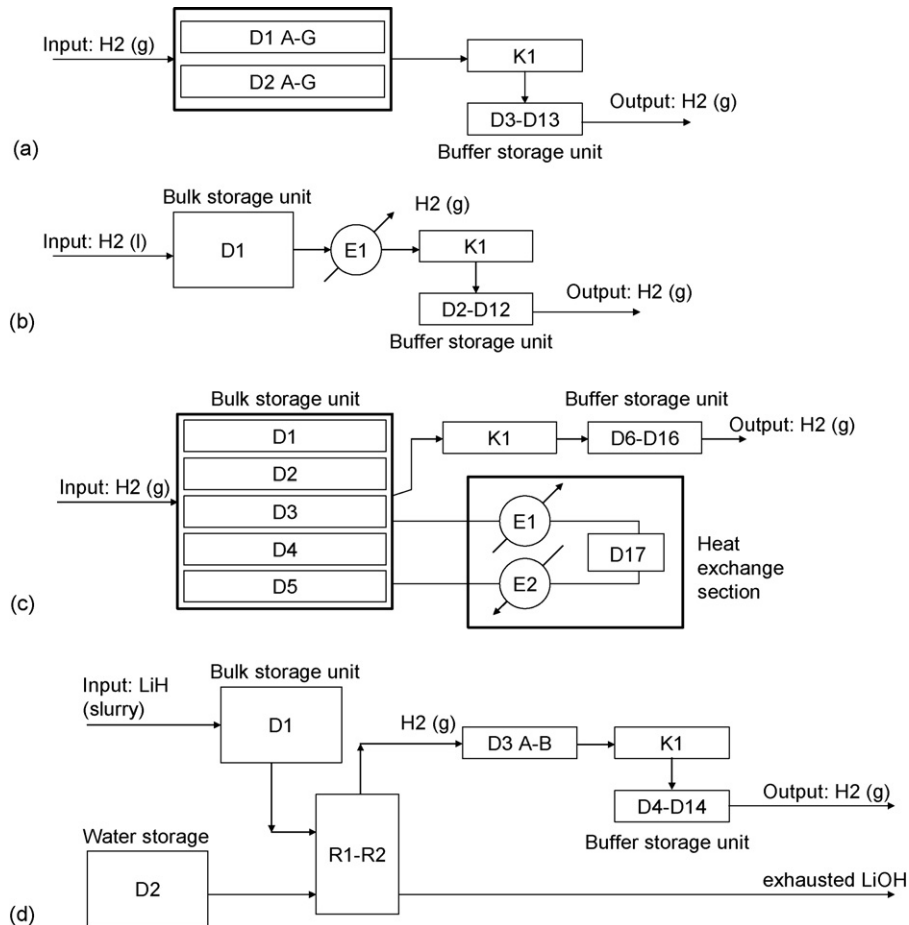
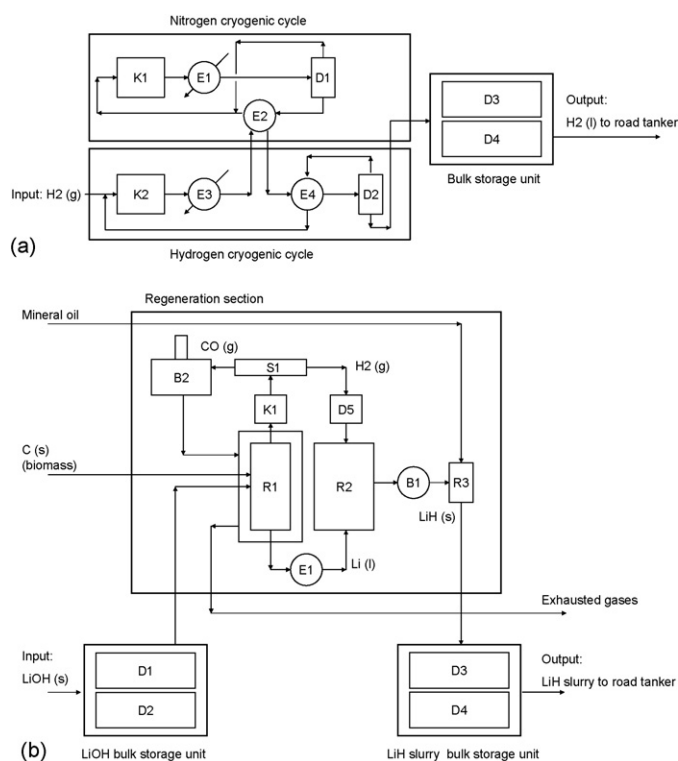


Fig. 3. Medium-scale hydrogen storage processes: reference schemes considered in the analysis. (a) Compressed, (b) cryogenic, (c) metal hydrides and (d) complex hydrides storage technologies.

**Table 4**  
Values of the unit KPIs calculated for the four alternative storage technologies considered

Scheme	Small scale				Medium scale				Large scale			
	Unit	Description	UPI	UHI	Unit	Description	UPI	UHI	Unit	Description	UPI	UHI
Com-pressed	D1–D2	Bulk storage tanks	$1.3 \times 10^3$	$1.7 \times 10^{-2}$	D1–D2 (A–G)	Bulk storage tanks	$7.3 \times 10^3$	$1.8 \times 10^{-2}$				
					D3–D13	Buffer storage tanks	$1.4 \times 10^3$	$1.9 \times 10^{-2}$				
					K1	Compressor	$1.1 \times 10^3$	$2.7 \times 10^{-1}$				
Cryo-genic	D1	Bulk storage tank	$6.0 \times 10^2$	$1.3 \times 10^{-1}$	D1	Bulk storage tank	$6.8 \times 10^3$	$2.0 \times 10^{-1}$	D1	N <sub>2</sub> Buffer storage tank	–	–
	E1	Electric vaporizer	–	–	D2–D12	Buffer storage tanks	$1.4 \times 10^3$	$1.9 \times 10^{-2}$	D2	Buffer storage tank	$1.6 \times 10^4$	$2.9 \times 10^{-2}$
					E1	Vaporizer	$9.4 \times 10^1$	$1.5 \times 10^{-2}$	D3–D4	Bulk storage tanks	$1.1 \times 10^6$	$1.2 \times 10^1$
					K1	Compressor	$1.1 \times 10^3$	$2.7 \times 10^{-1}$	K1	N <sub>2</sub> Compressor	–	–
									K2	Compressor	$5.9 \times 10^5$	$1.3 \times 10^2$
									E1	Heat exchanger	–	–
									E2	Heat exchanger	$7.8 \times 10^2$	$1.1 \times 10^0$
									E3	Heat exchanger	$6.8 \times 10^2$	$8.8 \times 10^{-3}$
								E4	Heat exchanger	$7.3 \times 10^2$	$5.6 \times 10^{-2}$	
Metal hydride	D1–D5	Bulk storage tanks	$1.8 \times 10^2$	$3.0 \times 10^{-3}$	D1–D5	Bulk storage tanks	$6.9 \times 10^2$	$1.7 \times 10^{-1}$				
	D6	Gas dispenser	$5.5 \times 10^1$	$1.0 \times 10^{-4}$	D7	Oil buffer tank	$1.1 \times 10^1$	$1.8 \times 10^{-3}$				
	D7	Oil buffer tank	$1.1 \times 10^0$	$2.0 \times 10^{-5}$	D6–D16	Buffer storage tanks	$1.4 \times 10^3$	$1.9 \times 10^{-2}$				
	E1	Heat exchanger	$3.7 \times 10^0$	$1.8 \times 10^{-2}$	E1	Heat exchanger	$5.5 \times 10^0$	$1.8 \times 10^{-2}$				
	E2	Heat exchanger	$3.4 \times 10^0$	$1.4 \times 10^{-2}$	E2	Heat exchanger	$6.5 \times 10^0$	$1.4 \times 10^{-2}$				
					K1	Compressor	$1.1 \times 10^3$	$2.7 \times 10^{-1}$				
Com-plex hydride					D1	Bulk storage tank	$1.5 \times 10^3$	$3.5 \times 10^{-2}$	D1–D2	Hydroxide storage tank	–	–
					D2	Water storage tank	–	–	D3–D4	Bulk storage tanks	$3.6 \times 10^3$	$7.3 \times 10^{-2}$
					D3 (A–B)	Collector tank unit	$5.5 \times 10^1$	$5.0 \times 10^{-5}$	D5	Buffer storage tank	$3.5 \times 10^2$	$2.7 \times 10^{-4}$
					D4–D14	Buffer storage tanks	$1.4 \times 10^3$	$1.9 \times 10^{-2}$	R1	Reactor for regeneration	$3.1 \times 10^3$	$1.8 \times 10^{-2}$
					R1–R2	Hydrolysis reactors	$5.3 \times 10^2$	$4.0 \times 10^{-3}$	R2	Reactor for hydride production	$1.7 \times 10^3$	$2.1 \times 10^{-2}$
					K1	Compressor	$1.1 \times 10^3$	$2.7 \times 10^{-1}$	R3	Mixer	$1.7 \times 10^3$	$1.4 \times 10^{-2}$
									E1	Lithium cooler	–	–
									K1	Compressor	$4.2 \times 10^3$	$6.4 \times 10^0$
									B1	Rotating furnace	$1.0 \times 10^3$	$8.2 \times 10^{-2}$
									B2	Furnace	–	–
								S1	Membrane separator	$2.0 \times 10^3$	$2.1 \times 10^{-1}$	



**Fig. 4.** Large-scale hydrogen storage processes: reference schemes considered in the analysis. (a) Cryogenic and (b) complex hydrides storage technologies.

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).

A similar procedure was applied to calculate the unit and the overall escalation hazard indexes. Similarly to UPI, the unit potential domino index, UPD, was defined as the square of the maximum escalation distance calculated for 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 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.

In the following, the eight KPIs listed in Table 2 were used to provide an overall quantification of the inherent safety of the alternative technologies proposed for hydrogen storage.

#### 4. Reference schemes for inherent safety comparison

Reference schemes were defined for the storage technologies considered in the present study. Figs. 2–4 report the reference schemes defined for the different technologies and the different scales considered in the assessment on the basis of literature data and of available information on existing hydrogen storage plants. The symbols used to identify the units in the figures are explained in Table 4.

Compressed gas storages were considered only for small- and medium-scale applications, since large-scale applications (according to the size definition reported in Section 2) are not of industrial interest. The reference schemes in Figs. 2(a) and 3(a) are based on high pressure bulk storage units (operating pressure was assumed, respectively, of 40 and 25 MPa).

Cryogenic storage units, containing liquid hydrogen at about 25 K, were considered for all the three scales. In small- and medium-scale applications, hydrogen should be delivered in the gas phase

to the user. Thus, in these cases, a vaporization section is needed. An electric heater (E1 in Fig. 2(b)) was considered for the small-scale scheme, while an external coil-vaporizer was considered for medium-scale applications (E1 in Fig. 3(b)). Large-scale cryogenic storage is coupled with a liquefaction plant, that was included in the analysis.

Metal hydrides storages (Figs. 2(c) and 3(c)), in which hydrogen is stored as adsorbed hydride on a specific support, are available for small-scale applications, and were considered also for medium-scale storage. Both processes are characterized by moderate pressure and temperature, respectively, 1.1 MPa and 350 K. Hydrogen is fed to the correspondent user in the gas phase. The

**Table 5**

Small-scale hydrogen storage schemes: calculated damage distances ( $d_{i,j,k}$ ) and credit factors ( $cf_{i,k}$ ) for each scenario ( $j$ ) of each LOC ( $i$ ) considered for each process unit ( $k$ )

Scheme	Unit	LOC	Scenario	$cf_{i,k}$	$d_{i,j,k}$ (m)			
Compressed	D1–D2: Bulk storage tanks	R1	JF	$1 \times 10^{-5}$	40.1			
			VE	$1 \times 10^{-5}$	18.2			
			FF	$1 \times 10^{-5}$	18.3			
		R2	JF	$5 \times 10^{-7}$	<5.0			
			R3	FB	$5 \times 10^{-7}$	21.0		
				VE	$5 \times 10^{-7}$	41.0		
		R3	FF	$5 \times 10^{-7}$	7.5			
			Cryogenic	D1: Bulk storage tank	R1	JF	$1 \times 10^{-4}$	24.4
		VE				$1 \times 10^{-4}$	29.4	
		FF				$1 \times 10^{-4}$	22.4	
R2	JF	$5 \times 10^{-6}$			<5.0			
	FF	$5 \times 10^{-6}$			<5.0			
	R3	FB			$5 \times 10^{-6}$	20.1		
VE		$5 \times 10^{-6}$			23.4			
Metal hydrides	E1: Electric vaporizer	D1–D5: Bulk storage tanks			R1	JF	$1 \times 10^{-3}$	5.9
						FF	$1 \times 10^{-3}$	5.6
						R2	JF	$5 \times 10^{-5}$
			FF	$5 \times 10^{-5}$	<5.0			
			R3	FB	$5 \times 10^{-5}$	6.5		
				VE	$5 \times 10^{-5}$	18.6		
				D6: Gas dispenser	R1	JF	$1 \times 10^{-5}$	7.6
			FF			$1 \times 10^{-5}$	<5.0	
			R2		JF	$5 \times 10^{-7}$	<5.0	
			R3		FB	$5 \times 10^{-7}$	12.4	
VE	$5 \times 10^{-7}$	9.2						
FF	$5 \times 10^{-7}$	<5.0						
D7: Oil buffer tank	R1	PF	$1 \times 10^{-5}$	5.9				
		FF	$1 \times 10^{-5}$	6.1				
	R2	FF	$5 \times 10^{-7}$	5.8				
		FF	$5 \times 10^{-7}$	5.9				
	E1: Heat exchanger	R4	PF	$1 \times 10^{-3}$	7.3			
			JF	$1 \times 10^{-3}$	8.5			
E2: Heat exchanger	R5	PF	$1 \times 10^{-4}$	6.5				
		PF	$1 \times 10^{-3}$	7.1				
	R4	PF	$1 \times 10^{-3}$	7.1				
		JF	$1 \times 10^{-3}$	8.1				
R5	PF	$5 \times 10^{-4}$	5.9					

For LOC and scenario definition see Table 6.

**Table 6**  
LOC events and scenarios considered in the consequence assessment procedure

LOC events	
R1	Small leak, continuous release from a 10 mm equivalent diameter hole
R2	Catastrophic rupture, release of the entire inventory in 600 s
R3	Catastrophic rupture, instantaneous release of the entire inventory and release from the full-bore feed pipe
R4	Pipe leak, continuous release from a hole having 10% of pipe diameter; heat exchanger small leak
R5	Pipe rupture, continuous release from the full-bore pipe; heat exchanger head full-bore rupture
Scenarios	
FB	Fireball
JF	Jet Fire
VE	Vapor Cloud Explosion
FF	Flash Fire
PF	Pool Fire
TD	Toxic Dispersion

heat exchange between the solid adsorption support, contained in the storage units (D1–D5 in Figs. 2(c) and 3(c)), and the thermal vector, is crucial. The use of a mineral oil as a thermal vector was considered, in order to remove the heat of adsorption and to provide the heat of desorption.

Complex hydrides were considered only for medium and large-scale application. Details on the process required for the formation

of the hydride and for the controlled release of hydrogen by its decomposition are reported in Appendix A. In medium-scale applications (Fig. 3(d)), it was assumed that only the decomposition would take place at the storage site, while the regeneration of the exhaust slurry would take place elsewhere (in a dedicated large-scale plant). Thus, in Fig. 3(d) the reaction of slurry, composed of a mineral oil and the hydride, with water was considered in order to release hydrogen. The bulk storage unit (D1) only contains the inert slurry at ambient pressure and temperature.

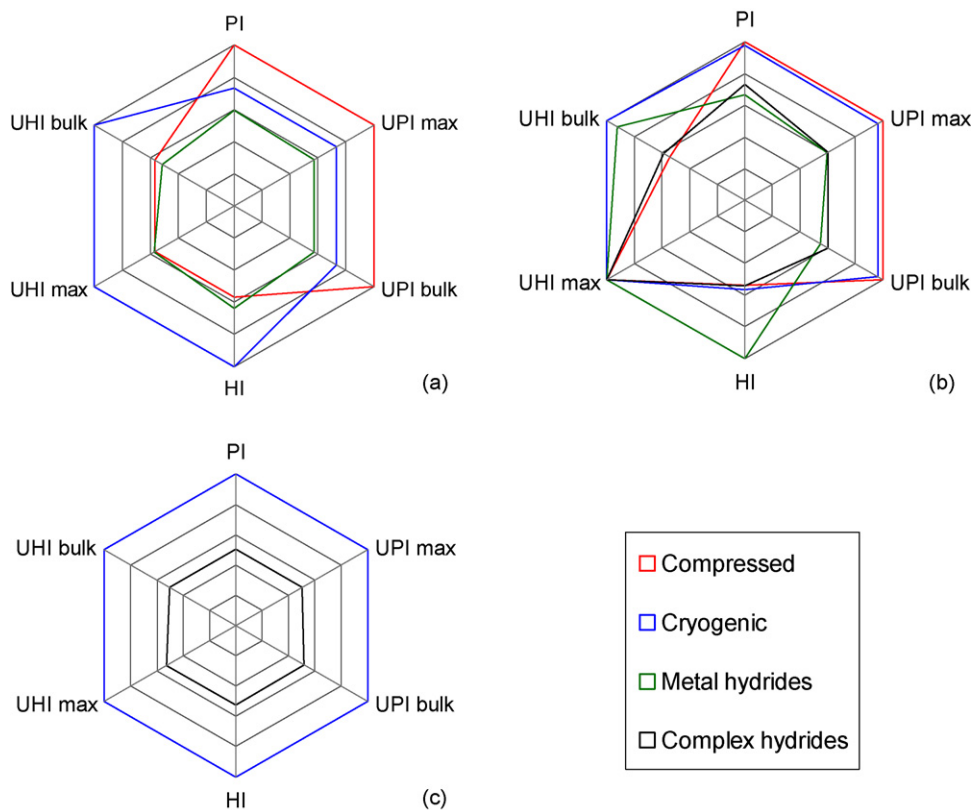
In the large-scale application (Fig. 4(b)), also the slurry regeneration unit was considered. The conversion from hydroxide to hydride involves high temperatures (1350 K) and is an endothermic process. Thus, an auxiliary heat source is needed (furnace B2 in Fig. 4(b)).

Further details on the reference schemes reported in Figs. 2–4 are provided in Appendix A.

## 5. Results and discussion

### 5.1. Small scale

Table 5 reports the damage distances, the escalation distances and the credit factors assessed for the “small-scale” reference schemes. Table 6 reports the definition of the LOC events and of the scenarios considered in the assessment.



**Fig. 5.** Normalized values of: overall potential hazard and inherent hazard indexes; unit potential hazard and inherent hazard indexes for the bulk storage unit; maximum unit potential hazard and inherent hazard indexes. (a) Small scale, (b) medium scale, and (c) large scale.

**Table 7**  
Overall inherent safety KPIs calculated for the for the four reference process schemes considered

Scheme	Small scale		Medium scale		Large scale	
	PI	HI	PI	HI	PI	HI
Compressed	$1.3 \times 10^3$	$1.7 \times 10^{-2}$	$9.8 \times 10^3$	$3.1 \times 10^{-1}$	$1.7 \times 10^6$	$1.4 \times 10^2$
Cryogenic	$6.0 \times 10^2$	$1.3 \times 10^{-1}$	$9.4 \times 10^3$	$5.0 \times 10^{-1}$		
Metal hydride	$2.4 \times 10^2$	$3.5 \times 10^{-2}$	$3.2 \times 10^3$	$4.9 \times 10^{-1}$		
Complex hydride			$4.6 \times 10^3$	$3.3 \times 10^{-1}$	$1.8 \times 10^4$	$6.8 \times 10^0$

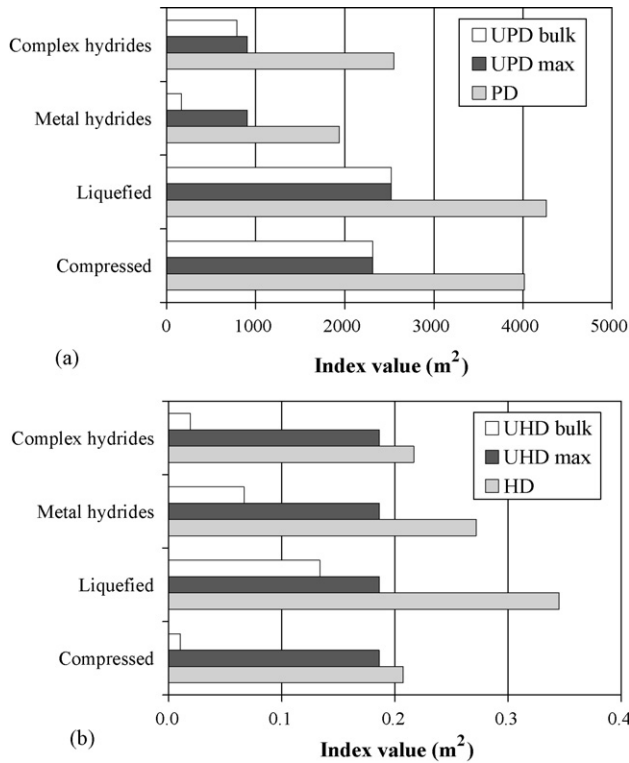


Fig. 6. Medium-scale hydrogen storage processes: overall, bulk storage and maximum unit values of domino potential (a) and inherent hazard (b) indexes.

The unit potential index was directly obtained from the data in Table 5 selecting the maximum damage distance for each unit, while the unit hazard index was calculated applying Eq. (1) to the same data. The results obtained are reported in Table 4. As shown in the table, in all the alternative schemes considered the hydrogen bulk storage is the unit that shows the higher value of the unit potential index, UPI. On the other hand, the introduction of credit factors in the analysis penalizes the presence of equipment items that may origin more easily LOC events. Thus, as shown in Table 4, in the case of metal hydrides the higher values of the unit hazard index, UHI, were obtained for the shell and tube heat exchangers.

Table 7 shows the values calculated for the overall potential and hazard indexes, PI and HI. The table evidences that the highest potential hazard index PI was obtained for the compressed gas storage, while the introduction of credit factors results in a penalization of the cryogenic technology, that results associated to the highest value of the hazard index, HI.

Fig. 5(a) reports a comparison among the normalized values of the potential and hazard indexes calculated for the alternative technologies. The radar plot allows an effective comparison among the expected safety performance of the alternative technologies. As shown in the plot, metal hydride technology shows the best expected safety performances. Compressed storage is the technology associated to the higher potential hazards. On the other hand, if credit factors are considered, liquefied storage is penalized, while compressed storage and metal hydrides are expected to have similar performances. This result is caused by the high credit factors associated to LOC events from auxiliary units, in particular heat exchangers, present in the metal hydrides scheme. These factors increase the overall hazard index associated to the technology, that results comparable to that of compressed storage, even if the UPI and UHI values of the bulk storage are much lower for metal hydrides than for compressed storage, as shown in Fig. 5(a).

Table 8

Medium-scale hydrogen storage—compressed scheme: calculated damage distances ( $d_{i,j,k}$ ), escalation distances ( $e_{i,j,k}$ ) and credit factors ( $cf_{i,j,k}$ ) for each scenario ( $j$ ) of each LOC ( $i$ ) considered for each process unit ( $k$ )

Unit	LOC	Scenario	$cf_{i,j,k}$	$d_{i,j,k}$ (m)	$e_{i,j,k}$ (m)
D1–D2: (A–G)	R1	JF	$1 \times 10^{-5}$	30.6	23.9
		VE	$1 \times 10^{-5}$	17.2	14.2
		FF	$1 \times 10^{-5}$	21.0	21.0
	R2	JF	$5 \times 10^{-7}$	33.0	24.6
		VE	$5 \times 10^{-7}$	17.3	14.2
		FF	$5 \times 10^{-7}$	15.8	15.8
	R3	FB	$5 \times 10^{-7}$	90.2	52.2
		VE	$5 \times 10^{-7}$	73.3	53.1
		FF	$5 \times 10^{-7}$	41.0	41.0
D3–D13	R1	JF	$1 \times 10^{-5}$	42.8	33.2
		VE	$1 \times 10^{-5}$	18.4	14.0
		FF	$1 \times 10^{-5}$	19.6	19.6
	R2	JF	$5 \times 10^{-7}$	5.2	<5.0
		VE	$5 \times 10^{-7}$	<5.0	<5.0
		FF	$5 \times 10^{-7}$	<5.0	<5.0
	R3	FB	$5 \times 10^{-7}$	28.1	16.1
		VE	$5 \times 10^{-7}$	21.4	15.5
		FF	$5 \times 10^{-7}$	10.4	10.4
K1	R4	JF	$1 \times 10^{-3}$	14.6	10.7
	R5	VE	$1 \times 10^{-4}$	38.8	35.1
	FF	$1 \times 10^{-4}$	30.1	30.1	

For unit labels definition see Table 4. For LOC and scenario definition see Table 6.

It must be remarked that the values of the credit factors used in the present study are derived from available literature data based on the analysis of standard equipment performances. Thus, in particular in the case of technologies still under development, as metal hydrides, the actual values of these factors in a future

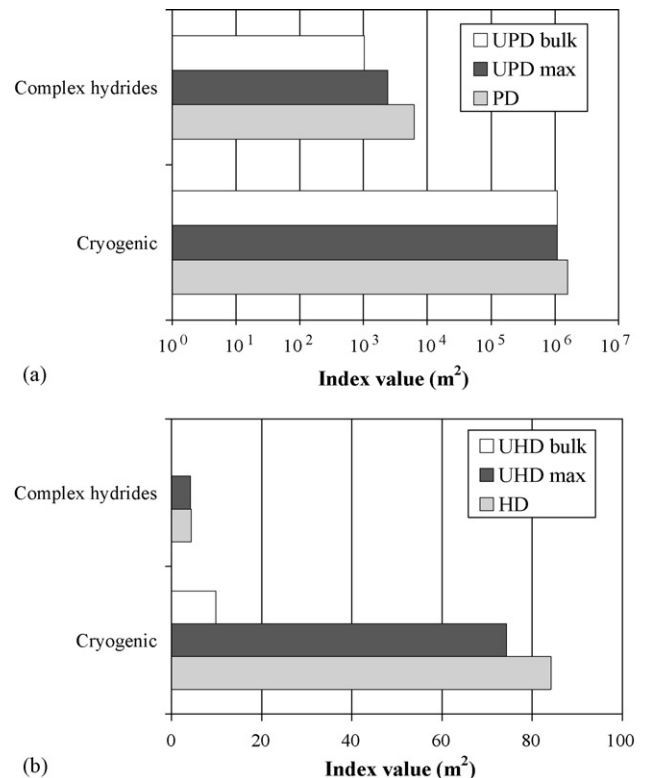


Fig. 7. Large-scale hydrogen storage processes: overall, bulk storage and maximum unit values of domino potential (a) and inherent hazard (b) indexes.



**Table 9**

Medium-scale hydrogen storage—cryogenic scheme: calculated damage distances ( $d_{i,j,k}$ ), escalation distances ( $e_{i,j,k}$ ) and credit factors ( $cf_{i,k}$ ) for each scenario ( $j$ ) of each LOC ( $i$ ) considered for each process unit ( $k$ )

Unit	LOC	Scenario	$cf_{i,k}$	$d_{i,j,k}$ (m)	$e_{i,j,k}$ (m)	
D1	R1	JF	$1 \times 10^{-4}$	24.4	18.5	
		VE	$1 \times 10^{-4}$	29.6	25.2	
		FF	$1 \times 10^{-4}$	22.4	22.4	
	R2	JF	$5 \times 10^{-6}$	35.4	26.7	
		VE	$5 \times 10^{-6}$	44.3	36.7	
		FF	$5 \times 10^{-6}$	30.6	30.6	
	R3	FB	$5 \times 10^{-6}$	87.3	51.8	
		VE	$5 \times 10^{-6}$	70.4	50.0	
		FF	$5 \times 10^{-6}$	55.2	55.2	
D2–D12	R1	JF	$1 \times 10^{-5}$	42.8	33.2	
		VE	$1 \times 10^{-5}$	18.4	14.0	
		FF	$1 \times 10^{-5}$	19.6	19.6	
	R2	JF	$5 \times 10^{-7}$	5.2	<5.0	
		VE	$5 \times 10^{-7}$	<5.0	<5.0	
		FF	$5 \times 10^{-7}$	<5.0	<5.0	
	R3	FB	$5 \times 10^{-7}$	28.1	16.1	
		VE	$5 \times 10^{-7}$	21.4	15.5	
		FF	$5 \times 10^{-7}$	10.4	10.4	
	E1	R4	FF	$1 \times 10^{-3}$	8.7	8.7
		R5	JF	$1 \times 10^{-5}$	14.7	11.4
			FF	$1 \times 10^{-5}$	10.1	10.1
K1	R4	JF	$1 \times 10^{-3}$	14.6	10.7	
	R5	VE	$1 \times 10^{-4}$	38.8	35.1	
		FF	$1 \times 10^{-4}$	30.1	30.1	

For unit labels definition see Table 4. For LOC and scenario definition see Table 6.

industrial application may be different, since specific equipment with improved safety performances may be used. Nevertheless, the results obtained evidence that in the perspective of an industrial implementation of this technology, the reliability of the auxiliary equipment will be an important issue to be addressed.

## 5.2. Medium scale

The values calculated for the unit potential and hazard indexes of “medium-scale” reference schemes are shown in Table 4. The values of damage distances and of credit factors used in the calculations are reported in Appendix A. The results evidence that, as in the previous case, the hydrogen bulk storage is the unit associated to the higher values of the potential index in all reference schemes, with the exception of that based on metal hydrides. In this case, the buffer tanks containing pressurized hydrogen show higher potential indexes than the bulk storage, due to the higher expected safety performance of bulk storage based on metal hydrides.

If the unit hazard indexes are compared, the hydrogen compressor always results the more hazardous unit. The credit factors related to this equipment item are particularly high, even if the damage distances are rather low with respect to those obtained for the bulk storage units. Thus, the compression units result the more critical with respect to inherent safety. Again, this is due to the importance given to the credit of LOC events in the unit hazard index (credit factors).

Table 7 reports the values of the overall indexes. The table evidences that the overall potential hazard index PI results higher for commercial technologies (compressed and liquefied storages) than for the innovative ones based on metal and complex hydrides. This is mostly due to the contribution of the bulk storage unit,

and is caused by the more severe operating conditions of this unit, that may result in worst consequences of the possible LOC events. From the point of view of inherent safety principles, these outcomes were expected, since the innovative technologies are examples of application of the principles underlying the “substitution” and “moderation” guidewords [16,17]. On the other hand, the higher values of the overall inherent hazard index HI were obtained for metal hydride and liquefied storage systems, while the HI value for compressed storage resulted lower and comparable to that obtained for the complex hydride system. A key issue that influences the values of the overall hazard index is 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 credit factors are associated to LOC events from these units. As a matter of fact, the introduction of credit factors in the analysis penalizes more complex designs, or the use of equipment items that more easily may origin LOC events. In particular, high values of the credit factor associated to the LOC events considered were obtained for the shell and tube unit present in the metal hydride reference scheme and for the multilayer coated vessel considered for cryogenic storage.

**Table 10**

Medium-scale hydrogen storage—metal hydrides scheme: calculated damage distances ( $d_{i,j,k}$ ), escalation distances ( $e_{i,j,k}$ ) and credit factors ( $cf_{i,k}$ ) for each scenario ( $j$ ) of each LOC ( $i$ ) considered for each process unit ( $k$ )

Unit	LOC	Scenario	$cf_{i,k}$	$d_{i,j,k}$ (m)	$e_{i,j,k}$ (m)
D1–D5 (tube side discharging)	R4	JF	$1 \times 10^{-3}$	16.7	12.5
		VE	$1 \times 10^{-3}$	8.4	<5.0
		FF	$1 \times 10^{-3}$	7.7	7.7
	R5	JF	$1 \times 10^{-5}$	31.3	16.1
		VE	$1 \times 10^{-5}$	19.0	9.2
		FF	$1 \times 10^{-5}$	18.0	18.0
D6–D16	R1	JF	$1 \times 10^{-5}$	42.8	33.2
		VE	$1 \times 10^{-5}$	18.4	14.0
		FF	$1 \times 10^{-5}$	19.6	19.6
	R2	JF	$5 \times 10^{-7}$	5.2	<5.0
		VE	$5 \times 10^{-7}$	<5.0	<5.0
		FF	$5 \times 10^{-7}$	<5.0	<5.0
	R3	FB	$5 \times 10^{-7}$	28.1	16.1
		VE	$5 \times 10^{-7}$	21.4	15.5
		FF	$5 \times 10^{-7}$	10.4	10.4
D17	R1	FF	$1 \times 10^{-5}$	8.3	8.3
	R2	JF	$1 \times 10^{-7}$	8.2	<5.0
E1	R4	JF	$1 \times 10^{-3}$	9.2	7.1
		FF	$1 \times 10^{-3}$	<5.0	<5.0
	R5	JF	$1 \times 10^{-5}$	12.4	10.1
		FF	$1 \times 10^{-5}$	7.8	7.8
E2	R4	JF	$1 \times 10^{-3}$	8.7	6.7
		VE	$1 \times 10^{-3}$	<5.0	<5.0
		FF	$1 \times 10^{-3}$	<5.0	<5.0
	R5	JF	$1 \times 10^{-5}$	13.1	11.3
		VE	$1 \times 10^{-5}$	7.8	5.4
		FF	$1 \times 10^{-5}$	8.3	8.3
K1	R4	JF	$1 \times 10^{-3}$	14.6	10.7
	R5	VE	$1 \times 10^{-4}$	38.8	35.1
		FF	$1 \times 10^{-4}$	30.1	30.1

For unit labels definition see Table 4. For LOC and scenario definition see Table 6.

**Table 11**

Medium-scale hydrogen storage—complex hydrides scheme: calculated damage distances ( $d_{i,j,k}$ ), escalation distances ( $e_{i,j,k}$ ) and credit factors ( $cf_{i,k}$ ) for each scenario ( $j$ ) of each LOC ( $i$ ) considered for each process unit ( $k$ )

Unit	LOC	Scenario	$cf_{i,k}$	$d_{i,j,k}$ (m)	$e_{i,j,k}$ (m)	
D1	R1	FB	$1 \times 10^{-4}$	17.7	13.0	
		VE	$1 \times 10^{-4}$	13.3	12.0	
		FF	$1 \times 10^{-4}$	<5.0	<5.0	
	R3	FB	$5 \times 10^{-6}$	44.2	33.1	
		VE	$5 \times 10^{-6}$	34.0	32.0	
		FF	$5 \times 10^{-6}$	11.2	11.2	
D2	–	–	–	–	–	
D3 (A–B)	R1	JF	$1 \times 10^{-5}$	<5.0	<5.0	
		FF	$1 \times 10^{-5}$	<5.0	<5.0	
	R2	JF	$5 \times 10^{-7}$	<5.0	<5.0	
		FF	$5 \times 10^{-7}$	<5.0	<5.0	
	R3	FB	$5 \times 10^{-7}$	12.4	<5.0	
		VE	$5 \times 10^{-7}$	9.2	8.0	
FF	$5 \times 10^{-7}$	<5.0	<5.0			
D4–D14	R1	JF	$1 \times 10^{-5}$	42.8	33.2	
		VE	$1 \times 10^{-5}$	18.4	14.0	
		FF	$1 \times 10^{-5}$	19.6	19.6	
	R2	JF	$5 \times 10^{-7}$	5.2	<5.0	
		VE	$5 \times 10^{-7}$	<5.0	<5.0	
		FF	$5 \times 10^{-7}$	<5.0	<5.0	
	R3	FB	$5 \times 10^{-7}$	28.1	16.1	
		VE	$5 \times 10^{-7}$	21.4	15.5	
		FF	$5 \times 10^{-7}$	10.4	10.4	
	R1–R2	R1	JF	$1 \times 10^{-4}$	<5.0	<5.0
			FF	$1 \times 10^{-4}$	<5.0	<5.0
		R2	VE	$5 \times 10^{-6}$	5.9	<5.0
FF			$5 \times 10^{-6}$	<5.0	<5.0	
R3		FB	$5 \times 10^{-6}$	28.1	11.0	
		VE	$5 \times 10^{-6}$	21.4	12.0	
FF	$5 \times 10^{-6}$	6.8	6.8			
K1	R4	JF	$1 \times 10^{-3}$	14.6	10.7	
		FF	$1 \times 10^{-4}$	30.1	30.1	
	R5	VE	$1 \times 10^{-4}$	38.8	35.1	
		FF	$1 \times 10^{-4}$	30.1	30.1	

For unit labels definition see Table 4. For LOC and scenario definition see Table 6.

The radar plot reporting the normalized values of the more significant hazard and potential indexes is shown in Fig. 5(b). The figure evidences that chemical and metal hydrides are expected to have better safety performances than the more conventional technologies for hydrogen storage. Again, the similar values of the hazard indexes obtained for the compressed storage and of metal and complex hydrides technologies evidence the problem of the reliability of auxiliary equipment as a key factor in the development of alternative technologies for hydrogen storage.

In medium-scale installations, escalation events may give an important contribution to the overall hazard. Fig. 6 reports the values calculated for the domino potential and hazard indexes. The values were calculated from the escalation distances and credit factors reported in Appendix A (Tables 8–11).

As shown in Fig. 6, cryogenic liquefied storage has very high values of both potential and hazard indexes, mainly due to the contribution of the hydrogen bulk storage. On the other hand, compressed storage has associated the higher potential index for domino effect, although credit factors are low, as shown in Fig. 6(b). Besides, alternative technologies present also in this case lower potential indexes (Fig. 6(a)) but, at the same time, the hazard

indexes result influenced by the compression unit. As a matter of fact, the maximum domino unit hazard index, UHD, is associated to this piece of equipment in all the assessed technologies.

### 5.3. Large scale

Table 4 reports the values calculated for the two large-scale hydrogen storage reference schemes considered in the present study. Also in this case, the data calculated for damage distances,

**Table 12**

Large-scale hydrogen storage—cryogenic scheme: calculated damage distances ( $d_{i,j,k}$ ), escalation distances ( $e_{i,j,k}$ ) and credit factors ( $cf_{i,k}$ ) for each scenario ( $j$ ) of each LOC ( $i$ ) considered for each process unit ( $k$ )

Unit	LOC	Scenario	$cf_{i,k}$	$d_{i,j,k}$ (m)	$e_{i,j,k}$ (m)
D1	–	–	–	–	–
D2	R1	JF	$1 \times 10^{-5}$	24.4	18.7
		VE	$1 \times 10^{-5}$	29.6	25.4
		FF	$1 \times 10^{-5}$	22.4	22.4
	R2	JF	$5 \times 10^{-7}$	41.2	30.0
		VE	$5 \times 10^{-7}$	45.5	38.8
		FF	$5 \times 10^{-7}$	34.7	34.7
	R3	FB	$5 \times 10^{-7}$	97.2	39.0
		VE	$5 \times 10^{-7}$	130.6	80.0
		FF	$5 \times 10^{-7}$	65.8	65.8
D3–D4	R1	JF	$1 \times 10^{-4}$	24.4	18.7
		VE	$1 \times 10^{-4}$	29.6	25.4
		FF	$1 \times 10^{-4}$	22.4	22.4
	R2	JF	$5 \times 10^{-6}$	207.4	143.1
		VE	$5 \times 10^{-6}$	230.3	192.3
		FF	$5 \times 10^{-6}$	157.6	157.6
	R3	FB	$5 \times 10^{-6}$	306.6	180.8
		VE	$5 \times 10^{-6}$	1035.5	875.0
		FF	$5 \times 10^{-6}$	1047.9	1047.9
E1	–	–	–	–	–
E2	R4	JF	$1 \times 10^{-4}$	12.0	<5.0
		VE	$1 \times 10^{-4}$	<5.0	<5.0
		FF	$1 \times 10^{-4}$	<5.0	<5.0
	R5	JF	$5 \times 10^{-6}$	19.7	7.6
		VE	$5 \times 10^{-6}$	32.9	10.0
		FF	$5 \times 10^{-6}$	13.0	13.0
E3	R4	JF	$1 \times 10^{-4}$	11.0	<5.0
		VE	$1 \times 10^{-4}$	<5.0	<5.0
		FF	$1 \times 10^{-4}$	<5.0	<5.0
	R5	JF	$5 \times 10^{-6}$	19.7	7.5
		VE	$5 \times 10^{-6}$	32.9	8.0
		FF	$5 \times 10^{-6}$	12.5	12.5
E4	R4	JF	$1 \times 10^{-4}$	19.4	<5.0
		VE	$1 \times 10^{-4}$	18.3	<5.0
		FF	$1 \times 10^{-4}$	16.5	16.5
	R5	JF	$5 \times 10^{-6}$	13.0	7.0
		VE	$5 \times 10^{-6}$	19.0	11.0
		FF	$5 \times 10^{-6}$	31.0	31.0
K1	–	–	–	–	–
K2	R4	JF	$1 \times 10^{-3}$	25.1	20.1
		VE	$1 \times 10^{-3}$	16.5	13.2
		FF	$1 \times 10^{-3}$	13.2	13.2
	R5	JF	$1 \times 10^{-4}$	478.8	300.0
		VE	$1 \times 10^{-4}$	771.1	404.0
		FF	$1 \times 10^{-4}$	707.1	707.1

For unit labels definition see Table 4. For LOC and scenario definition see Table 6.

**Table 13**

Large-scale hydrogen storage—complex hydrides scheme: calculated damage distances ( $d_{i,j,k}$ ), escalation distances ( $e_{i,j,k}$ ) and credit factors ( $cf_{i,k}$ ) for each scenario ( $j$ ) of each LOC ( $i$ ) considered for each process unit ( $k$ )

Unit	LOC	Scenario	$cf_{i,k}$	$d_{i,j,k}$ (m)	$e_{i,j,k}$ (m)
D1–D2	–	–	–	–	–
D3–D4	R1	FB	$1 \times 10^{-4}$	22.2	10.0
		VE	$1 \times 10^{-4}$	16.8	11.0
		FF	$1 \times 10^{-4}$	<5.0	<5.0
	R3	FB	$5 \times 10^{-6}$	65.1	27.0
		VE	$5 \times 10^{-6}$	51.6	37.0
		FF	$5 \times 10^{-6}$	17.3	17.3
D5	R3	FB	$5 \times 10^{-7}$	23.8	9.6
		VE	$5 \times 10^{-7}$	18.1	13.0
		FF	$5 \times 10^{-7}$	8.3	8.3
R1	R3	FB	$5 \times 10^{-6}$	28.5	17.5
		VE	$5 \times 10^{-6}$	60.3	41.0
		FF	$5 \times 10^{-6}$	14.2	14.2
R2	R3	FB	$5 \times 10^{-6}$	46.6	15.3
		VE	$5 \times 10^{-6}$	40.0	33.0
		FF	$5 \times 10^{-6}$	16.5	16.5
R3	R3	FB	$5 \times 10^{-6}$	45.7	24.0
		VE	$5 \times 10^{-6}$	37.9	18.7
		FF	$5 \times 10^{-6}$	11.2	11.2
E1	–	–	–	–	–
K1	R4	JF	$1 \times 10^{-3}$	70.0	54.0
		VE	$1 \times 10^{-3}$	37.7	33.0
		FF	$1 \times 10^{-3}$	35.8	35.8
	R5	JF	$1 \times 10^{-4}$	46.6	31.0
		VE	$1 \times 10^{-4}$	19.1	15.3
		FF	$1 \times 10^{-4}$	11.0	11.0
B1	R1	JF	$1 \times 10^{-3}$	<5.0	<5.0
		FF	$1 \times 10^{-3}$	13.1	13.1
	R3	FB	$5 \times 10^{-5}$	37.2	21.0
		VE	$5 \times 10^{-5}$	28.7	16.0
		FF	$5 \times 10^{-5}$	9.3	9.3
		–	–	–	–
S1	R1	TD	$1 \times 10^{-4}$	50.0	–
		JF	$1 \times 10^{-4}$	9.0	6.0
		FF	$1 \times 10^{-4}$	10.0	7.0

For unit labels definition see Table 4. For LOC and scenario definition see Table 6.

escalation distances and credit factors are reported in Appendix A. Table 4 evidences that in both processes the hydrogen bulk storage unit does not result the more critical item. Nevertheless, both the unit potential and unit hazard indexes are much lower for the complex hydride bulk storage, as evidenced also in the radar plot reported in Fig. 5(c). This is due to the inherently safer storage of hydrogen as stable hydride in solid phase in this technology. Thus, the results obtained for the bulk storage indexes are a concrete example of the effectiveness of the application of the “substitution” and “moderation” inherent safety guidewords for hazard reduction [17].

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. As shown in Table 4, in both alternatives the compression unit gives the more important contribution to both the potential and the hazard indexes.

The overall potential and hazard indexes reported in Table 7 evidence that the expected safety performance of the complex hydrides large-scale storage including the regeneration section results higher than that of conventional cryogenic liquid storage including a liquefaction section. As shown in Table 7 and in Fig. 5(c), both potential and inherent hazard indexes, PI and HI, evaluated for the cryogenic storage result about two orders of magnitude higher than in the alternative technology. Similar results were obtained for the escalation hazard, as shown in Fig. 7. The PD index evaluated for the cryogenic alternative is strongly influenced by the bulk storage unit while the HD index, that takes into account the credit factors, is penalized also in this case by the hydrogen compression unit. Similarly, the escalation hazard KPIs evaluated for the complex hydrides technology result about two order of magnitude lower than those of the liquefied storage process. Is it worth to notice that in the case of escalation hazards, the contribution of the membrane separation unit (labelled as S1 in Fig. 4(b)) to the overall index is much lower than in the case of hazards to humans, since the toxic dispersion of carbon monoxide is not taken into consideration as in the case of potential and inherent hazard indexes (see Tables 4 and 7).

## 6. Conclusions

The expected safety performances of alternative hydrogen storage technologies were explored estimating several KPIs based on consequence assessment and credit 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 safety issues to be considered in the further development and in the possible industrial implementation of these technologies. All the comparative analysis indicated that the potential hazard is always lower for the innovative technologies proposed for hydrogen storage. This is mainly a consequence of the application of principles underlying the inherent safety “substitution” guideword, since in these alternative technologies hydrogen is stored as a less hazardous hydride. Moreover, metal hydrides and complex hydrides storage systems present less severe operative conditions than those of conventional technologies (inherent safety guideword “moderation”). Nevertheless, if the credit factors of LOC events are considered, based on standard equipment reliability data, the innovative technologies, and in particular metal hydrides storage, show lower safety performances than conventional storage processes. As a matter of fact, Table 7 shows that the ranking based on the hazard index (HI) is in the reverse order with respect to that based on the potential index (PI). This is due to the more complex storage process, requiring a higher number of auxiliary units, and to the credit of LOC events in standard units as compressors or shell and 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.

## Appendix A

### A.1. Description of reference technologies

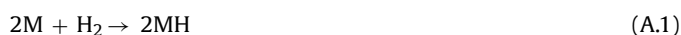
Techniques based on hydrogen compression [8] are widely used due to their simplicity and to the lower cost of small-scale storage and transport of hydrogen gas. However, this technique presents higher costs in large-scale applications and the safety of pressurized cylinders is of big concern, in particular in densely populated regions [2]. Operating pressures range from 20 to 40 MPa in ordi-

nary cases and further applications will require operating pressures up to 70 MPa. The gas is stored at ambient temperature.

Liquefied hydrogen storage has a higher volumetric and gravimetric hydrogen density compared to the other techniques [8]. However, a large amount of energy is required to liquefy the gaseous hydrogen (about 30% of the energy content of the storage). 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, since temperatures are very low (20–25 K).

The techniques based on hydrogen storage materials, such as metal and complex hydrides, provide a hydrogen storage vessel volumetrically effective compared with compressed hydrogen gas, increasing the safety quality aspects, due to the inherently less severe operative conditions [1,2,8,13–15].

Several metals or alloys can be used to store hydrogen by the formation of metal hydrides [11,13–15], as shown in Eq. (A.1):

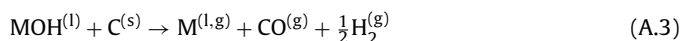


where M is a common metal. It is well-known that several inter-metallic alloys are capable of absorbing and releasing hydrogen without compromising their own structure. Manipulation of absorption temperature or supply pressure can influence the storage capacities and absorption rates. Similarly, desorption rates can also be controlled by varying the desorption temperatures. As an example, in the case of  $\text{La-Ni}_5$  hydride, the isothermal adsorption point is at 350 K and 1.1 MPa [11,13–15].

Besides metal hydrides, other storage materials are under development, based on hydrolysis of particular inorganic compounds identified as the complex hydrides [2,14]. Complex hydrides are inorganic solids, such  $\text{LiH}$ ,  $\text{CaH}_2$ ,  $\text{NaBH}_4$ , etc. which strongly react with water to produce hydrogen following the Eq. (A.2):



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



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

## A.2. Reference schemes

“Small-scale” storages are devoted to automotive applications. The PFDs for the proposed technologies are reported in Fig. 2. A 5 kg storage on board was considered for all the alternative technologies, supplying gaseous hydrogen at a fuel cell engine on the vehicle. The fuel cell operating pressure was supposed to be 0.3 MPa, which is a typical operating condition for these equipment items. In the case of the gaseous storage (Fig. 2(a)), the high pressure hydrogen is delivered from the cylinders D1 and D2 by pressure gradient. In the case of the liquefied storage at 25 K (Fig. 2(b)), an electric vaporizer E1 provides low pressure gaseous hydrogen. Finally, in the case of the metal hydrides storage, a battery of 5 tanks (D1–D5) is used, each containing up to 1 kg hydrogen via adsorption on a specific metal support (Fig. 2(c)). An organic oil is used as a thermal vector, both to provide and subtract heat from the bulk storage unit in the different operating conditions. In the loading phase, the adsorption heat is removed and the oil is cooled in the E2 heat exchanger. In the discharging phase, the oil heated in E1 heat exchanger, provides the desorption heat to the storage unit. The released hydrogen is stored in a pressurized buffer D6.

“Medium-scale” storages are mainly developed in the perspective of application to hydrogen refuelling stations. In most applications, the storage unit is supposed to contain about 500 kg of hydrogen, stored using different alternative technologies. In the case of the gaseous storage technology, the bulk storage was considered at an operating pressure of 25 MPa (Fig. 3(a)) with 2 commercial tube trailers (D1 and D2). Each trailer was considered as composed of 6 pressurized cylinders, each containing about 40 kg of hydrogen. Since for the refuelling of the next generation hydrogen vehicles high pressures will be required, a compressor (K1) coupled with a buffer storage unit (D3–D13) is needed, providing gaseous hydrogen at 35 MPa.

In the case of the cryogenic storage (Fig. 3(b)), hydrogen is stored at 20–25 K at moderate pressure (0.6 MPa). An external finned tubes heat exchanger (E1) is needed to provide gaseous hydrogen. Also in this case, the coupled compression (K1)–high pressure buffer (D2–D12) units are needed.

The medium-scale reference scheme for metal hydrides storage technology (Fig. 3(c)) was based on the same principle of the small-scale scheme. Each unit was supposed to store up to 100 kg hydrogen by adsorption on metal hydrides. In the discharge phase, hydrogen is released at low pressure (about 1.1 MPa) and compressed as in previous cases.

The medium-scale reference scheme for hydrogen storage on complex hydrides (Fig. 3(d)) consists in three main sections: (i) a bulk storage unit for the hydride, at atmospheric pressure and ambient temperature; (ii) a reaction section, in which the gaseous hydrogen is produced; (iii) a compression and buffer storage unit. The hydride is dispersed in a mineral oil in order to prevent the contact with moisture, which may cause unwanted hydrogen release. In the reaction section, the slurry is mixed with water and gaseous hydrogen is released via hydrolysis. Gaseous hydrogen is then compressed (K1) and sent to the high pressure buffer (D4–D14). Two semi-batch reactors are supposed to work alternatively, in order to allow continuous supply of hydrogen to the compression unit.

As discussed above, in “large-scale” reference schemes, also auxiliary sections were considered in order to obtain a correct representation of the expected safety performance of the process. Thus, a liquefaction section was considered together with cryogenic storage, and a hydroxide regeneration section was associated to the complex hydrides storage.

In large-scale cryogenic storage reference scheme (Fig. 4(a)), a double tank bulk storage unit (D3 and D4) was considered, containing 27 t of liquid hydrogen at 1.7 MPa and 20–25 K. The liquefaction process is characterized by the coupling of two cycles, respectively, for nitrogen and hydrogen liquefaction. In each cycle, the gas is compressed (compressors K1 and K2, respectively), then cooled (heat exchangers E1–E4) and finally expanded and liquefied. The liquid is separated from the vapor in a buffer flash chamber (respectively, D1 and D2), and the vapor is recycled to the compressor.

Also in the case of the complex hydrides reference scheme (Fig. 4(b)), two large tanks (D3 and D4) were considered for the bulk storage, containing 90 t of hydride slurry, equivalent to 27 t of hydrogen. A  $\text{LiH}$  slurry with mineral oil was considered as a support for hydrogen storage. The hydrogen release section is the same illustrated for the medium-scale storage. In the regeneration section, carbon based material (e.g. biomass) is mixed with the exhaust hydroxide supplied from the exhaust storage (D1 and D2 tanks). In a decomposition reactor (R1), the reduction of the hydroxide was considered. The gases formed are extracted and compressed (K1). Hydrogen is separated via membrane separation (S1) and coupled in the mixer R2 with the liquid lithium coming from R1 to give the regenerated hydride, which is separated (B1) and mixed with the

mineral oil (R3). The heat necessary is provided by the combustion of auxiliary fuel and waste carbon monoxide gas coming from S1 in burner B2.

### A.3. Damage distances, escalation distances and credit factors

The detailed results of the consequence analysis for medium and large-scale reference schemes are reported in Tables 8–13. The tables include the damage distances ( $d_{i,j,k}$ ), escalation distances ( $e_{i,j,k}$ ) and the correspondent credit factors ( $cf_{i,k}$ ) calculated for each scenario of each process unit following the procedure described in Section 3. The definitions of the LOC events and of the scenarios considered are reported in Table 6.

## References

- [1] M. Conte, P.P. Proisini, S. Passerini, Overview of energy/hydrogen storage: state-of-the-art of the technologies and prospects for nanomaterials, *Mater. Sci. Eng. B* 108 (2004) 2–8.
- [2] L. Zhou, Progress and problems in hydrogen storage methods, *Renew. Sustain. Energy Rev.* 9 (2005) 395–408.
- [3] M. Conte, A. Iacobazzi, M. Ronchetti, R. Vellone, Hydrogen economy for a sustainable development: state-of-the-art and technological perspectives, *J. Power Sources* 100 (2001) 171–187.
- [4] A. Sarkar, R. Banerjee, Net energy analysis of hydrogen storage options, *Int. J. Hydrogen Energy* 30 (2005) 867–877.
- [5] R.D. Venter, G. Pucher, Modelling of stationary bulk hydrogen storage systems, *J. Hydrogen Energy* 22 (1997) 791–798.
- [6] L.C. Cadwallader, J.S. Herring, Safety issues with hydrogen as a vehicle fuel, INEEL/EXT-99-00522 Report, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID, 1999.
- [7] B.R. Kinzey, A. Ruiz, P.B. Davis, The Hydrogen safety program of the U.S. Department of Energy, in: *Proc. of the 1st International Conference on Hydrogen Safety*, Pisa, 2005.
- [8] N. Takeichi, H. Senoh, T. Yokota, H. Tsuruta, K. Hamada, H.T. Takeshita, H. Tanaka, T. Kiyobayashi, T. Takano, N. Kuriyama, Hybrid hydrogen storage vessel, a novel high-pressure hydrogen storage vessel combined with hydrogen storage material, *Int. J. Hydrogen Energy* 28 (2003) 1121–1129.
- [9] A. Domashenko, A. Golovchenko, Y. Gorbatsky, V. Nelidov, B. Skorodumov, Production, storage and transportation of liquid hydrogen. Experience of infrastructure development and operation, *Int. J. Hydrogen Energy* 27 (2002) 753–755.
- [10] F. Mitlitsky, A.H. Weisberg, B. Myers, Vehicular hydrogen storage using lightweight tanks, in: *Proc. of the 2000 US DOE Hydrogen Program Review*, NREL/CP-570-28890, Washington, DC, 2001.
- [11] M.T. Hagstrom, P.D. Lund, J.P. Vanhanen, Metal hydride hydrogen storage for near-ambient temperature and atmospheric pressure applications, a PDSC STUDY, *Int. J. Hydrogen Energy* 20 (1995) 897–909.
- [12] W. Clark, J. Rifkin, T. O'Connor, J. Swisher, T. Lipman, G. Rambach, Clean hydrogen science and technology team, hydrogen energy stations: along the roadside to the hydrogen economy, *Utilities Policy* 13 (2005) 41–50.
- [13] D. Browning, P. Jones, K. Packer, An investigation of hydrogen storage methods for fuel cell operation with man-portable equipment, *J. Power Sources* 65 (1997) 187–195.
- [14] R. Aiello, M.A. Matthews, D.L. Reger, J.E. Collins, Production of hydrogen gas from novel chemical hydrides, *Int. J. Hydrogen Energy* 24 (1999) 1123–1130.
- [15] D.M. Mahmut, Y. Kaplan, Numerical study of hydrogen absorption in an Lm–Ni<sub>5</sub> hydride reactor, *Int. J. Hydrogen Energy* 26 (2001) 957–963.
- [16] T.A. Kletz, What you don't have, Can't leak, *Chem. Ind.* 6 (1978) 287–292.
- [17] CCPS, *Inherently Safer Chemical Processes—A Life Cycle Approach*, AIChE, New York, 1996.
- [18] P.A.M. Uijt de Haag, B.J.M. Ale, *Guidelines for Quantitative Risk Assessment (Purple Book)*, Committee for the Prevention of Disasters, The Hague (NL), 1999.
- [19] American Petroleum Institute, *Risk-based Inspection Base Resource Document*, API standard 581, first ed., API, Washington, DC, 2000.
- [20] C. Delvosalle, C. Fievez, A. Pipart, B. Debray, ARAMIS project: a comprehensive methodology for the identification of reference accident scenarios in process industries, *J. Hazard. Mater.* 130 (2006) 200–219.
- [21] A. Tugnoli, V. Cozzani, G. Landucci, A consequence based approach to the quantitative assessment of inherent safety, *AIChE J.* 53 (2007) 3171–3182.
- [22] C.J.H. Van Den Bosh, R.A.P.M. Weterings, *Methods for the Calculation of Physical Effects (Yellow Book)*, third ed., Committee for the Prevention of Disasters, The Hague, 1997.
- [23] F.P. Lees, *Loss Prevention in the Process Industries*, second ed., Butterworth - Heinemann, Oxford, 1996.
- [24] V. Cozzani, G. Gubinelli, E. Salzano, Escalation thresholds in the assessment of domino accidental events, *J. Hazard. Mater.* 129 (2006) 1–21.
- [25] V. Cozzani, A. Tugnoli, E. Salzano, Prevention of domino effect: from active and passive strategies to inherently safe design, *J. Hazard. Mater.* 139 (2007) 209–219.