SAFETY ASPECTS RELATED TO THE UNDERGROUND HYDROGEN STORAGE

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ABSTRACT

The transition from fossil fuels to the renewable energies (wind, solar) is a key factor to face climate change and build a sustainable, reliable, and secure energy system. To balance the intermittent energy demand and supply affecting the renewable sources, the surplus of electrical energy may be converted in hydrogen and then storage in geological formations. While the risks associated to the natural gas storage in the sub-surface are well known from decades, those associated with hydrogen underground storage (UHS) are relatively underexplored. This paper presents an inventory of risks related to large H_2-storage in depleted gas and oil fields, salt caverns and aquifers. Different issues such as integrity and durability of materials, H_2 leakages and interaction with the reservoir, H_2 uncontrolled outflow from the wellhead with potential combustion of air-hydrogen mixture (fire and explosion), soil subsidence and induced seismicity, are analyzed.

1.0 INTRODUCTION

With the "European Green Deal" the EU has adopted a set of initiatives to face the climate changes, based on a competitive and efficient economy, with the goal of net zero greenhouse gas emissions by 2050 and a reduction of at least 55 % compared to 1990 levels by 2030 ("Fit for 55" package) [1]. In this context, hydrogen is considered as an important option for the economy decarbonisation, particularly, if produced from renewable energy sources. To underline the importance of hydrogen in the Community energy strategies, in July 2020 a path was outlined with the aim to install at least 6 GW of electrolysers green hydrogen in the EU by 2024 and 40 gigawatts by 2030 [2]. Hydrogen has also the potential role to support the penetration of non-programmable renewable energy sources by the conversion of the electric overgeneration through storage options (power-to-gas), improving the safety and resilience of the energy system. Among the different storage methods, the geological one offers the best prospects even if there are still technological, legislative, and regulatory barriers that need appropriate insights. In fact, while the risks associated with underground gas storage (UGS) are well-known from decades of operation, those related to underground hydrogen storage (UHS) are relatively underexplored. The present paper gives an overview of risks related to the H_2 large storage in depleted gas and oil fields, salt caverns and aquifers. After a description of the general aspects related to UHS in section 2, the fundamental chemical and physical H_2 properties for the underground storage are presented in section 3. In section 4, the main safety issues related to UHS are described in terms of: hydrogen impact on the material integrity and durability, H_2 leakages (above and below the ground), uncontrolled H_2 release from the wellhead (blow-out), H_2 interaction with the reservoir, soil subsidence and induced seismicity. Finally, conclusions are reported in section 5.

2.0 UNDERGROUND HYDROGEN STORAGE

2.1 General aspects

Hydrogen is an attractive energy storage option with its a high heating value (120 - 140 MJ/kg) and clean combustion products. Nowadays, it is mainly produced either via natural gas (steam methane reforming) using fossil fuel feedstock (blue and grey hydrogen), with an energy efficiency of 65–85%, or by water electrolysis with an energy efficiency of 55%–75% [3] [4]. While the blue H_2 production is considered clean because the produced CO_2 can be sequestered, other processes leading to grey H_2

production are not environmentally friendly as they often contain impurities such as CH_4, Ar, CO, CO_2, and N_2 [5]. H_2 has a low density (0.084 kg/m^3 at 293.15 K and 101325 Pa), and for that reason large volumes, much beyond the scope of surface-based storage facilities, are required to store energy in the scale of GWh to TWh. Using geological formations such as salt caverns, aquifers, depleted oil and gas fields, large scale (G–TWh) of energy in the form of H_2 can be stored since these sites provide huge volumes for storing this gas at high pressure (high energy densities).

The underground storage has shown over time to offer lot of advantages in terms: (i) safety - underground facilities are less susceptible to fire, terrorist attacks or military actions; (ii) storage volumes - traditional surface tanks would have to cover extensive areas to store the same amounts of gas as in underground facilities; (iii) economy - the costs of UGS construction are much lower than those of surface facilities with a comparable capacity; (iv) availability of suitable geological sites - these are common in many countries and over large areas. In the recent years, the availability and storage capacity of geological sites has grown significantly, especially in northern hemisphere countries. As of January 2010, 642 storage sites have been surveyed, mainly as depleted hydrocarbon oil and gas fields (476), while the remaining are aquifers (82) and salt caverns (76) [6]. Most of the sites are in North America (399) and Canada (50); there are 130 sites in Europe, 50 sites in countries under the former USSR (CIS), 12 sites in Asia and Oceania and 1 site in South America. In 2015, the global storage capacity was approximately 413 billion m^3, with 110 billion m^3 within the European countries as follows: depleted hydrocarbon fields 68%, aquifers 15%, salt caverns 17% [6].

As a result of the international interest on UHS, initiatives have been funded to investigate the viability of this technology. In 2012, the European Union launched several research projects, in support to its strategy for the economy decarbonization, such as the HyUnder project (2012) aimed to provide the first European-wide assessment of the potential for hydrogen storage in salt caverns to renewable electricity over the long term [7]. In the same years, at the Sandia National Laboratory, a research program, funded by US Government, on flexibility of the UHS in depleted oil and natural gas fields was launched (2009) [8]. In Germany, three different projects were activated through the Federal Ministry for Education and Research: H2STORE (2013) aimed to study the storage in depleted gas fields [9], InSpEE (2015) on the use of digital technologies for storage monitoring [10], ANGUS+ (2017) focused on geological storage modeling, risk-assessment techniques, and experimental studies to assess the impact of chemical and microbiological effects on the thermal storage [11]. More recently, the following projects were activated: HESTOR (2019) on the geological storage in salt caverns [12], HyStorPor (2022), developed at the Edinburgh University, on the geological storage in porous structures [13], HyStoreIES (2020), co-funded by the European Union, on the geological storage in aquifers and depleted fields [14] and SHASTA (2022), coordinated by the United States Department of Energy (DoE), focused on subsurface hydrogen and natural gas storage [15]. Since 2022, the International Energy Agency (IEA), through the Technology Collaborative Programme, is coordinating a three-year program (2022-2024) aimed at demonstrating the technical-economic and social feasibility of the UHS [16].

2.2 Underground H_2 storage options

For the UHS different sites can be useful for this purpose: salt caverns, depleted hydrocarbon (natural gas and petroleum) fields and aquifers. Salt caverns (artificial chambers created in salt deposits) are frequently used to store high pressure natural gas. These sites offer a high seal, high stability of the structure over time, chemical inertia toward the stored gases, less prone to the development of in-situ microbiological activities [17]. Example of UHS in salt caverns have been realized at Kiel (Germany), Teesside in Yorkshire (England), and in Texas (USA) [18].

Depleted hydrocarbon fields, traditionally used for the storage of natural gas, are made up of porous and permeable rocks [6]. These sites are easier to use and manage as they have proven structural integrity and retention capacity, as well as offering the advantage of using pre-existing surface infrastructures and reducing the technical and economic resources for their exploitation. On the other hand, the presence of residues such as oil can compromise, over time, the hydrogen purity by triggering chemical reactions (conversion of H_2 to CH_4) or by residues dispersion in the gas volume.

At the Diadema site, Patagonia (Argentina), a pilot injection of hydrogen into a sandstone geological structure, associated with the natural gas storage, was realised [18].

Aquifers are porous and permeable rock formations which have the pore space occupied by fresh or saline water (at greater depths). They are common in all sedimentary basins all over the world and they may be an alternative for UHS in those areas where depleted hydrocarbon fields or salt caverns are not available [6]. Examples of UHS in aquifers were realised at the sites of Beynes (France), Ketzin (Germany) and Lobodice (Czech) [18]. An example of sites considered for the UHS is reported in Table 1.

Tab. 1 – Sites considered for the UHS [18].

Site name	Since (years)	Type	% H_2	P, T	Depth (m)
Kiel (Germany)	1971	Salt cavern	60-64	8-10 MPa	1330
Teesside (UK)	1972	Salt cavern	95	5 MPa	400
Texas (USA)	-	Salt cavern	95	-	
Beynes (France)	1956	aquifer	50	-	430
Ketzin (Germany)	1971	aquifer	62	-	200 –250
Lobodice (Czech)	1989	aquifer	50	9 MPa, 307 K	430
Diadema (Argentina)	-	Natural gas	10	1 MPa, 323 K	600

2.3 Energy cycles associated with underground H_2 storage

In general, four types of UHS can be distinguished depending on the form of the energy initially produced, the form of the final energy consumed, the methods of energy conversion, and the combination between these elements [18].

Underground storage of pure hydrogen. The final use of this hydrogen is in fuel cells, for the conversion into electricity, where a high degree of purity is required (e.g., electric mobility). The most suitable place for the storage of high purity hydrogen are saline caverns which are high seal, have a high degree of purity and are characterized by a low risk of contamination with other impurities [18]. The energy cycle uses the excess electric generation from renewable source plants (wind, photovoltaic), to produce hydrogen through the chemical electrolysis of water (see Figure 1). This hydrogen is finally extracted from the salt caverns in periods of high energy demand and then converted back into electricity.

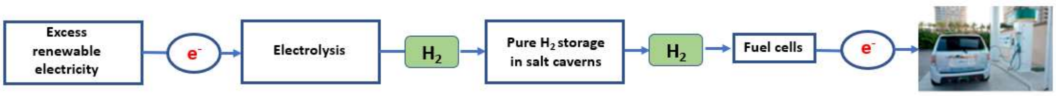

Figure 1 – Energy cycle associated with the underground storage of pure H_2.

Underground storage of a mixture of natural gas and hydrogen in low concentrations. Hydrogen produced by electrolysis of water is mixed (blending), in low concentrations, with natural gas (a mixture containing more than 90% of CH_4) and then injected into the reservoir [18]. Currently, the industry uses mixtures of natural gas with hydrogen in low concentration (6-15%) such a way this storage method does not cause a significant change in the energy content of the stored gas; moreover, due to the low H_2 concentration, once the mixture has been extracted from the reservoir, this option offers the advantage to possibly re-use the existing infrastructure of the gas network so avoiding the risks of the H_2 interaction with steel e.g., embrittlement. In this energy cycle, hydrogen is used as fuel and the technology is known as power-to-gas (see Figure 2).

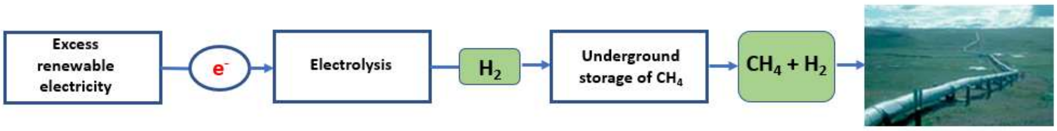

Figure 2 - Energy cycle associated with the underground storage of CH_4 and H_2 at low concentrations.

Underground storage of a mixture of H_2, CO, CH_4 and CO2 (syngas and town gas). Syngas is a mixture of H_2 (20-40%) with CO, while town gas is a mixture of H_2 (50-60%), CO and CH_4. CO is seen as an energy vector in both cases but with less potential than hydrogen, while the amount of CO_2 largely depends on the production technique. This mixture is produced through the coal gasification obtained by injecting steam at 1073 K and oxygen. The latest versions of coal gasification technology allow to have hydrogen up to 70% in the mixture which can then be used for (i) electricity generation in gas turbines and (ii) as fuel for lighting or heating in the case of town gas. The energy cycle consists of the coal gasification to produce syngas or town gas, the storage in the reservoir (aquifers, salt caverns or depleted hydrocarbon fields), the conversion in electricity in gas turbines or direct use as a fuel (see Figure 3) [18].

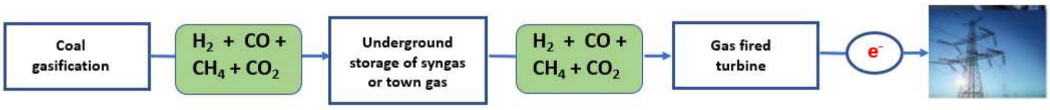

Figure 3 – Energy cycle associated with the underground storage of syngas or town gas.

Biological methanation through underground storage. The injection of a mixture of H_2 and CO_2 into an aquifer or depleted gas field produces, in the presence of bacteria, CH_4 through the Sabatier's reaction (methanogenesis). The objective of this storage mode is to enrich the potential energy of the gas by generating methane [18]. The process, induced by bacteria at low temperatures, can be economically favorable compared to industrial ones that operate at high temperatures and require the use of expensive catalysts for the reaction. The resulting gas can then be injected into the gas network as fuel as long as the residual fraction of CO_2 is minimized (see Figure 4).

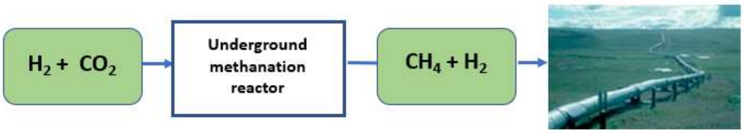

Figure 4 – Energy cycle associated with the biological methanation via underground storage.

3.0 FUNDAMENTAL H_2 PROPERTIES FOR UNDERGROUND STORAGE

Physical and chemical properties of H_2 are the main drivers for achieving a successful storage. Hydrogen is a diatomic gas with a density of 0.084 kg/m^3 at normal temperature and pressure conditions[1] (NTP). As shown in Table 2, H_2 is about 8 times less dense than CH_4 (0.668 kg/m^3) so that more space and pressure will be required for H_2 to store the same mass amount of gas. The diffusion coefficient in air of H_2 (0.61 cm^2/s) is around 4 time higher compared to CH_4 (0.16 cm^2/s), due to small size of its molecule, so it diffuses in solids faster than other gases. Due to the low

[1] Temperature and pressure of 293.15 K and 101325 Pa, respectively.

dynamic viscosity, H_2 could results in leakage because it remains highly diffusive when injected in the reservoir at high pressure as compared to CH_4. For all these reasons, the reservoir to be used for hydrogen storage will require a higher sealing capacity in comparison to those used for methane.

Like any other fuel, H_2 is flammable and potentially dangerous, and it shares many similarities with natural gas as both are lighter than air. In comparison with CH_4, hydrogen has wider flammability limits, lower minimum ignition energy and lower flashpoint temperature and therefore more prone to ignite when released in air (see Tab. 2). On ignition methane radiates heat and creates a flame that is clearly visible; ignited hydrogen on the other hand radiates little (infrared) heat (IR) but emits substantial UV (ultraviolet) radiation [20]. The lack of IR gives little sensation of heat but the exposure to a hydrogen flame still causes severe burns because of the UV radiation. Because a hydrogen flame is also not easily detectable (contrary to methane), risks associated with hydrogen burning are increased. In case of leakage of hydrogen or methane in confined spaces, where leakage can remain undetected, or in case of large volume releases, there is an elevated risk of explosion both hydrogen and methane. However, the effects of a hydrogen explosion are different compared to methane: when a mixture of hydrogen and air explodes, the higher flame propagation speed potentially generates high pressures that could result in massive damage, while when a mixture of methane and air explodes, the potential for burst damage is lower [21].

Table 2 – Physical and chemical properties of H_2, CH_4 affecting the underground storage [6] [17] [19].

Property	Hydrogen (H_2)	Methane (CH_4)
Molecular weight (kg/kmole)	2.02	16.0
Density @ NTP [kg/m^3]	0.084	0.668
Dynamic viscosity @ NTP [x10^{-5} Pa s]	0.88	1.10
Diffusion coefficient in air @ NTP [cm^2/s]	0.61	0.16
Solubility in water [mg/ml]	0.0016	0.023
Heating value [MJ/kg]	120 – 141.7	50 – 55.5
Flammability range in air [vol%] (LFL & UFL)	4.0 - 75	5.3 - 15
Flash point [K]	20	85
Minimum ignition energy @NTP [mJ]	0.02	0.29
Burning velocity in air @ NTP [m/s]	2.6 – 3.2	0.37 – 0.45

4.0 SAFETY ASPECTS RELATED TO UHS

4.1 General consideration

The identification of potential critical issues related to the UHS is of great importance for the implementation of adequate prevention and mitigation measures, in the perspective of limiting, in case of accident, the consequences for people, environment and infrastructures. It is worthwhile to remember that any investigation aimed at identifying the main risks associated UHS cannot ignore the experience gained, over time, with the UGS. In order to improve our understanding of the risks associated with UHS, a qualitative non site-specific comparison can be outlined with the UGS, primarily based on differences in gas properties. With this approach, the potential risks related to the UHS are classified as follows [15] [18] [22]: (i) integrity of materials; (ii) H_2 leakages; (iii) uncontrolled H_2 release from the wellhead (blow-out); (iv) H_2 interactions with reservoir (v) subsidence and induced seismicity.

4.2 Integrity of materials

Piping and surface infrastructures. The surface infrastructures of a storage plant include several components (compressors, heat exchangers, dryers) and piping systems for the connection to the gas network. Many studies have shown that existing natural gas pipelines to and from the reservoir can potentially be reused for the transport of hydrogen at low concentrations, with a positive impact on the cost related to the hydrogen integration in the energy system [22]. However, the integrity of materials used for piping can be reduced if exposed to high hydrogen concentrations, at high pressures, for long periods [23]. In fact, it is well known that hydrogen can influence the fatigue properties of steels by favoring the propagation of cracks as well as the performance of some plastics used in valve seals [20]. As regard as the surface infrastructures used for the operation of the UHS, it is believed that these can be very similar to those already used for natural gas; moreover, the operating conditions of the UHS are similar to those adopted for UGS. Even if hydrogen has been produced on an industrial scale for decades (e.g., starting from natural gas, through the steam reforming process), transported (via pipes) and mainly used in the petrochemical industry, in complete safety way, its use as pure or blended with natural gas (blending) on some components of the surface infrastructures, can be a critical issue. For instance, particular attention should be paid to the operation of compressors whose performance can be degraded due to compatibility of materials with hydrogen or due to the occurrence of possible leakages through the seals [24]. In the case of mixtures with a high hydrogen content (indicatively for concentrations above 10%), modifications must be foreseen for the impellers of compressors already used for natural gas, preferring the use of reciprocating compressors over mechanical ones, as they are more suitable with this gas. Therefore, the reuse of existing UGS surface infrastructures, with pure or hydrogen at high concentrations, is not straightforward and adaptation and/or replacement of specific components should be planned.

Well. As a primary pathway between the surface and the subsurface (underground storage complex) well integrity is an important source of risk. Well must withstand the stresses during operating conditions and always maintain its structural integrity. Therefore, well materials must be compatible with hydrogen and with any compounds that can be produced in the reservoir (e.g., H_2S) as result of chemical and microbiological reactions of hydrogen with minerals. Because many of well materials are steel alloys, these must be compatible with hydrogen over a wide range of gas concentrations, temperatures, and pressures; all these parameters, together with the stress state of the material, are responsible for the steel embrittlement, steel blistering as well as cracks development (see Figure 5). The low-carbon steels often used in wells are susceptible to H_2-mediated failure; variable compositions steels and degassing treatments are considered for mitigation of embrittlement reactions [20]. Microbially-induced corrosion of steel in the environmental created by the introduction of H_2 to the reservoir, can be also another element of risk [15].

Cement. Another material widely used for the construction of the well is the cement that usually fills the anulus between the well and the adjacent rock (see Figure 5). One of the main challenges for the well integrity is to prevent fluid or gas migration through the porous cement; for this reason, cement must be chemically resistant to hydrogen and have low permeability to avoid the gas diffusion through into the rock formation [22]. In addition, it must be able to withstand repeated cyclic loads during the operational phases of the reservoir.

Elastomer. In the UGS industry, elastomers are used to seal the annulus between tubing (pipe where gas is injected or withdrawn) and casing (see Figure 5). There are H_2-resistant sealing elements already used in the H_2-industry; it remains to investigate whether commonly used elastomers in UGS wells can resist the diffusion of H_2. Hydrogen permeation into these seals elements may increase the rate of degradation and result in a loss of integrity with a potential rapid decompression of the well

[22].

4.3 H_2 leakages

Leakage from the well. Safety against hydrogen leakages from the well is ensured by multiple barriers which can be classified into primary as the Surface-controlled Subsurface Safety Valve (SSSV), and secondary as the automatic gate valves at the wellhead. The long experience gained by the oil & gas industry, the availability of new technologies and guidelines, the improvements made in the design and testing phases of the components, have substantially reduced the frequency of well failure [25]. However, up to now, there are doubts about the possibility to fully use the same wells of the oil & gas industry for the UHS. In fact, the small size of the hydrogen molecule, its high diffusivity, combined with hydrogen embrittlement properties, can facilitate the gas dissolution in the materials used for the well. This could result in higher leakage probabilities of hydrogen compared to natural gas when using the existing UGS materials and related infrastructures [26].

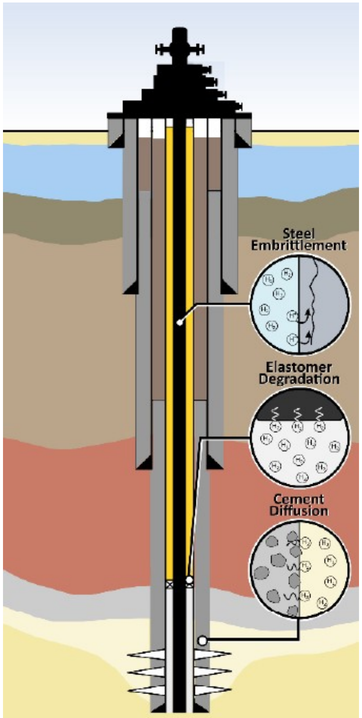

Figure 5 – Cross section view of a well for UHS. Main phenomena affecting the well integrity: steel embrittlement, cement diffusion, and elastomer degradation [15].

Leakage from subsurface. To avoid any hydrogen leakages, reservoirs must have specific retention characteristics. Salt caverns with both low permeability and porosity are considered impermeable and therefore capable of retaining natural gas and hydrogen [7]. As regards the depleted hydrocarbon fields, such as those of natural gas, they are certainly suitable for safely storage of large volumes of gas; in fact, they have proven their great sealing capacity over millions of years. However, due to the peculiar chemical-physical properties of hydrogen, the use of depleted hydrocarbon fields should be evaluated on a case-by-case basis. Furthermore, in the case of unforeseen geological pathway the probability of hydrogen leakages from the site could increase.

Leakage detection. In the event of leakage at the surface, the incipient detection is essential to limit the consequences and the potential impact on the health, environment, and infrastructures. It should be reminded that both methane and hydrogen are difficult to perceive by our senses as they are both colorless, odorless, tasteless. The methane detection was solved by mixing the gas with odorants;

unfortunately, these odorants do not work with hydrogen due to its extreme volatility (high buoyancy) which tends rapidly to rise upwards and separate from them [20]. The problem of gas leakage detection was solved in the oil & gas industry through various devices such as, ultrasonic gas leakage detector, infrared gas detectors, flame detectors. However, hydrogen leakages need of specific sensors to be detected. In fact, the hydrogen flames are difficult to detect being practically invisible so specific flame detectors are used such as thermal detectors, ultraviolet (UV) detectors and/or multi-spectral infrared (IR) detectors, which have the capability to detect electromagnetic radiation in the non-visible spectrum [20]. As far as the leakages from the reservoir are concerned, these are difficult to detect although the pressure in the geological reservoir is continuously monitored; in fact, these leakages are usually small compared to the stored gas volume and the related pressure changes are difficult to measure.

Leakage consequences. In general, leakages have a different impact depending on whether they occur near the surface or at depth and on the nature of the gas (methane or hydrogen). As far as methane is concerned, in the first case, the gas that migrates to the surface can pose a risk for health, environmental and safety of infrastructure as it can generate toxic clouds with risk of suffocation or combustion phenomena (fires, explosions); in the second case, methane can migrate toward other geological formations, contaminating the groundwater, with the risk to be still released into the atmosphere [22]. In both scenarios, risks for health and environment are combined with the economic risk (gas leakage) as well as reputational damage and reduced public support to the UGS. In case of hydrogen release into an unconfined open environment, a faster dispersion in the atmosphere occurs compared to methane so that gas accumulation and combustion, in presence of ignition source, are less likely. Conversely, if hydrogen is accumulated in a confined space, the risk of combustion is greater than with methane, as hydrogen is more prone to ignition and have a wider flammability range. In presence of high congestion and confinement, due to the higher burning velocity of hydrogen in air, deflagration could also turn into detonation, with the generation of pressure peaks and massive damages [20].

4.4 Uncontrolled H_2 release form the wellhead (blow-out)

The worst-case scenario includes the uncontrolled gas release from the well (blow-out) with flow rates of order of tens to hundred kg/s. The consequences coming from the blow-out of the well strongly depend on the nature of the gas. For the hydrogen, due to its wide flammability range and the low value of the minimum ignition energy, there is a high probability that the scenario will evolve with the ignition of gas (this is not necessarily the case of methane). If the prompt ignition occurs, what is generated is a jet-fire, while in the case of delayed ignition and generation of flammable gas-air cloud, a flash-fire or an explosion can occur. However, the quantities of hydrogen released from the well can be limited if the SSSV valve is correctly installed in the well, which being of the failsafe type can automatically interrupt the gas flow from the reservoir, at the first stage of the accident at the surface. As far as the consequences are concerned, these cannot disregard from the following aspects: (i) nature of the gas (pure H_2 or H_2-CH_4 mixture), (ii) gas release condition and dispersion in the environment (flow rate and atmospheric conditions), (iii) presence of toxic and/or corrosive compounds formed inside and outside the reservoir (e.g., H_2S, SO_2), (iv) extension of combustion area, i.e. flame length and thermal impact for a jet-fire, or (v) overpressure peaks for an explosion [27].

4.5 H_2 interactions with the reservoir

The small size of the hydrogen molecule allows the gas to be three times more diffusive into solids than methane. For the storage in porous media enriched in water, such as aquifers or depleted hydrocarbon fields, the process of gas dissolving in the liquid is the predominant effect. In the aquifers, the hydrogen loss is low compared to methane (hydrogen solubility in water is 13 times lower than methane) while in depleted hydrocarbon fields the situation changes as the water is already saturated with methane, and hydrogen losses can occur because the methane in the brine are expected to be substituted with hydrogen [22]. Other problems due to the H_2 interaction with the reservoir concern the loss or contamination of gas as result of geo-biochemical reactions. More specifically, these reactions can cause [15]:

- contamination of stored H_2 by production of other gases (e.g., H_2S);
- mineral dissolution/precipitation leading to increased or reduced injectivity;
- accelerated growth of the microbial population able to clog well pipes;
- mineral dissolution affecting mechanical properties of the reservoir.

Any of these changes could compromise H_2 storage security and UHS efficiency [15]. The kinetics of the geo/biochemical reactions and the nature of the reagents/microbiological population are the driving factors for the development and subsequent release of potentially harmful products from the reservoir. In general, high temperatures, pressures and salinity levels can increase microbial activity and the rate of some chemical reactions [22]. The development of chemical reactions and microbial activity is believed to be less important in salt caverns, due to the lower water content, lower microbiological activity and mineral concentration, compared to depleted hydrocarbons fields and aquifers.

Most of the redox reactions driven by hydrogen do not occur at low temperatures and without catalysts, due to the apolar nature of the molecule and its high binding energy (436 kJ/kg). However, in the case of geological storage, some hydrogen-induced redox reactions, able to modify the stored gas quality, are also possible at low temperatures; this is the case of the hydrogen reaction with pyrite minerals (FeS_2), just above the 323 K, to form pyrrhotite (FeS) and hydrogen sulfide (H_2S) [22] [15]. Generated H_2S can modify redox potential and the PH of water, causing additional fluid-rock interactions. It can also compromise the well/field infrastructure due to its flammable, corrosive, and toxic nature. A second mechanism driving the hydrogen sulfide formation is related to the bacteria which can reduce, at temperatures above 365 K, the SO_4^{2-} ion to H_2S in the presence of hydrogen [22]. However, it should be reminded that there is an ample experience with H_2S; in fact, the oil & gas industry, for many years now, is capable to manage the risk associated with the H_2S by specific resistant materials (duplex stainless steel) and the adoption of specific safety measures (e.g., H_2S detectors).

Another important issue for the operation of depleted hydrocarbon fields is that related to the reduction of the porosity and permeability of the rock following the triggering of chemical-physical reactions and biological processes (pore clogging) [28]. The reduction of the porosity can also occur due to microbial growth and bacterial accumulation, processes that can be accelerated by the presence of nutrient-rich water or organic material (biological clogging) [29]. The triggering of hydrogeochemical reactions can lead to chemical clogging by the precipitation of minerals (e.g., calcite, gypsum, phosphates, and oxides); also, H_2S can induce the precipitation of ferrous compounds which can modify the material porosity of reservoir [22]. For all these reasons, before to perform any hydrogen injection in the reservoir, laboratory tests aimed at investigating the mineralogical, chemical-physical, and microbiological characteristics of the subsoil and possible hydrogen / rock /fluid interactions, at typical storage conditions of temperature and pressure, should be included.

4.6 Subsidence and induce seismicity

The triggering of the ground subsidence and induced seismicity is another potential risk associated with UHS. As far as the subsidence at surface is concerned, it is known as it can induced by the extraction of natural gas and salt from the subsoil. In the case of salt caverns, the extension and the rate of subsidence depend on the rate of salt creep, that is a function of the salt type, the pressure and temperature in the reservoir; for porous deposits, the amount and speed at which subsidence proceeds is a function of the rock compaction, which depends on the pressure in the deposit, the friction angle, type of rock and on the properties of the surrounding geological formations [22].

Experience with induced seismic events at UGS is very limited. Of the more than 640 UGS facilities operating worldwide, only one has been shut down due to seismic concerns, the Castor Project off the coast of the Valencia Gulf, Spain [15]; another documented case of induced seismicity at UGS facilities occurred in The Netherlands [22]. In depleted hydrocarbon fields, induced seismicity can be generally caused by a reduction of the pressure inside the deposit with a differential compaction of the overlaying mass and faults formation to absorb vertical movement; this movement along faults, which commonly occurs abruptly, potentially causes earthquakes (induced seismicity). Similarly, the pressure inside the reservoir should not exceed the maximum pressure (lithostatic pressure) to avoid fracturing of the rock. It is believed that if a similar safety approach for the UHS is used as for UGS i.e., the operating pressure in the reservoir is maintained withing a prescribed range, no specific differences in terms of induced seismicity can be highlighted between the two underground storage options. As far as the saline caverns, the possibility that stress states in the material can lead to the formation of cracks is relatively low since the salt has a viscoplastic behavior, i.e., it tends to deform rather than break so the likelihood of induced seismicity can be assumed to be very low.

5.0 CONCLUSIONS

Energy storage is considered to be a key factor in the energy supply chain for the 21th century because it can increase the use of renewable energy sources, enhance the grid stability, improve the efficiency of the energy system and reduce the use of fossil fuels. Large-scale geological H_2 storage offers the capacity to balance inter-seasonal supply/demand discrepancies, de-couple energy generation from demand, thus supporting decarbonization of the entire energy system. Despite the consolidated experience acquired by the oil & gas industry in the operation of natural gas fields, the chemical-physical properties of hydrogen pose new problems and challenges to the underground storage. The assessment of potential risks related to the subsurface large-H_2 storage such as leakages from the well and reservoir, uncontrolled release from the wellhead, the interaction of hydrogen with structural materials and rock matrix, is a prerequisite for the implementation of safe operating conditions in the underground storage, health and environment protection, and a conscious acceptance of this technology by the public.

ACKNOWLEDGMENTS

This work has been financed by the Research Fund for the Italian Electrical System under the Three-Year Research Plan 2022-2024 (DM MITE n. 337, 15.09.2022), in compliance with the Decree of April 16th, 2018”.

REFERENCE

1. EUROPEAN COMMISSION, The European Green Deal, COM (2019) 640 final, Brussels, 2019.
2. EUROPEAN COMMISSION, A hydrogen strategy for a climate-neutral Europe, COM (2020) 301 final, Brussels, 2020.
3. Amid, A., Mignard, D., Wilkinson, M., Seasonal storage of hydrogen in a depleted natural gas reservoir, *Int. J. Hydrogen Energy*, 41, 2016, pp. 5549–5558.
4. Gahleitner, G., Hydrogen from renewable electricity: An international review of power-to-gas pilot plants for stationary applications, *Int. J. Hydrogen Energy* 38, 2013, pp. 2039–2061.
5. Laban, M.P., Hydrogen storage in salt caverns: Chemical modelling and analysis of large-scale hydrogen storage in underground salt caverns, Delft University of Technology, 2020.
6. Tarkowski, R., Underground hydrogen storage: Characteristics and prospects, *Renewable and Sustainable Energy Reviews*, 105, 2019, pp. 86-94.
7. HyUnder. Assessing the potential, actors and business models of large-scale underground hydrogen storage in Europe, 2015, Available: http://hyunder.eu/.
8. Lord, A.S., Overview of geologic storage of natural gas with an emphasis on assessing the feasibility of storing hydrogen, Sandia National Laboratories, Albuquerque, 2009.
9. Pudlo, D., The H2STORE project: Hydrogen underground storage - a feasible way in storing electrical power in geological media?, Clean Energy Systems in the Subsurface: Production, Storage and Conversion, Springer Series in Geomechanics and Geoengineering, 2013, pp. 395-412.
10. Information system salt structures: planning basis, selection criteria and estimation of the potential for the construction of salt caverns for the storage of renewable energies (hydrogen and compressed air) (InSpEE), BGR, 2015, Available: https://www.bgr.bund.de/EN
11. Kabuth, A., Dahmke, A., Beyer, C., Energy storage in the geological subsurface: dimensioning, risk and spatial planning: the ANGUS+ project, *Environmental Earth Sciences*, vol. 76:23, 2017.
12. HESTOR - Energy storage in the form of hydrogen in salt caverns, ENTSOG, 2019, Available: https://www.entsog.eu/hydrogen?page=2.
13. HyStorPor, University of Edinburgh, 2022. [Online]. Available: https://blogs.ed.ac.uk/hystorpor/
14. Hydrogen Storage In European Subsurface, 2020, Available: https://hystories.eu/
15. Subsurface Hydrogen and Natural Gas Storage: State of Knowledge and Research recommendations Report, SHASTA: Subsurface Hydrogen Assessment, Storage and Technology Acceleration Project, DOE/NETL-2022/3236.
16. IEA, Hydrogen TCP - Task 42: Underground Hydrogen Storage, 2022, Available: https://www.ieahydrogen.org/task/task-42-underground-hydrogen-storage/#
17. Muhammed, N. S., Haq, B., Al Shehri, D., A review on underground hydrogen storage: Insight into geological, *Energy Reports*, 8, 2021, pp. 461-499.
18. Panfilov, M., Underground and pipeline hydrogen storage, *Compendium of Hydrogen Energy*, Elsevier, 2015, pp. 92-116.
19. Tarkowski, R., Uliasz-Misiak, B., Tarkowski, P., Storage of hydrogen, natural gas, and carbon dioxide – Geological and legal conditions, *International Journal of hydrogen energy,* 46, 2021, pp. 20010-20022.
20. Polidoro, F., Manzini, G., Individuazione dei principali scenari di rischio caratterizzati dal rilascio di idrogeno da impianti di stoccaggio o trasporto, Ricerca di Sistema, RSE, n.210011648, Milano, 2021.
21. Molkov, V., Fundamentals of Hydrogen Safety Engineering I, bookboon.com, 2015.

22. V. der Valk, K., Unen, M., Brunner, L., Groenenberg, R., Inventory of risks associated with underground storage of compressed air (CAES) and hydrogen (UHS), and qualitative comparison of risks of UHS vs. underground storage of natural gas (UGS), TNO, 2020.
23. Melaina, M. W., Antonia, O., Penev, M., Blending hydrogen into natual gas pipeline networks: a review of key issues, NREL/TP-5600-51995, 2013.
24. Gonzalez-Diez, N., Van der Meer, S., Bonetto, J., Herwijn, A., North Sea Energy D3.1 Technical assessment of hydrogen transport, compression, processing offshore, As part of Topsector Energy:TKI Offshore Wind & TKI New Gas, NSE3-D3.1, 2020.
25. Bèrest, P., Reveillere, A., Evans, D., Stower, M., Review and analysis of historical leakages from storage salt caverns well, *Oil & Gas Science and Technology*, 74, 2019, pp.27.
26. H2tools, Energy, U.S. Department of Energy's Office of Energy Efficiency and Renewable, 2022, Available: www.h2tools.org.
27. Portarapillo, M., Di Benedetto, A., Risk Assessment of the Large-Scale Hydrogen Storage in Salt Caverns, *Energies*, vol. 14, No. 2856, 2021.
28. R. G., Maliva, Clogging in anthropogenic aquifer recharge, *Springer Hydrogeology*, 2020.
29. National Research Council, Prospects for managed underground storage of recoverable water, Division on Earth and life studies, water science and technology board, Committee on Sustainable Underground Storage of Recoverable Water, 2008.