Literature Review - Underground Hydrogen Storage

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Abstract

The growing popularity of green or clean hydrogen as a means of achieving zero-emission targets has led to extensive research and development efforts aimed at bridging the gap between laboratory projects and real-world applications. However, the production and storage of hydrogen pose various technological challenges, including the primary fuel used for production, cost, and energy density. Green hydrogen can be produced through electrolysis of water or hydrogen production with Carbon capture and storage (CCS), utilizing excess renewable energy from sources such as wind and solar, which can be stored as hydrogen to prevent seasonal and weather fluctuations. This report provides an in-depth overview of the current state-of-the-art in the field of the hydrogen economy, including the properties of hydrogen necessary for storage and technological advancements such as cryogenic tanks and underground geological storage.

Steam methane reforming is currently the most common method of hydrogen production, but it relies on natural gas as a feedstock, which is a finite resource and a significant source of greenhouse gas emissions. Electrolysis is a promising alternative that can use renewable energy sources to produce hydrogen, but it currently requires significant investments in infrastructure and improvements in efficiency. Biomass gasification is another alternative that can use renewable resources such as agricultural waste to produce hydrogen.

Each type of storage facility has its own advantages and challenges, and the choice of which type to use will depend on factors such as the application, cost, and efficiency of the technology. Compressed hydrogen storage is a well-established technology that is suitable for a range of applications, but it requires high-pressure vessels that can be expensive to manufacture and maintain. Liquid hydrogen storage offers a high energy density, but it requires cryogenic temperatures and can be challenging to handle and transport. Hydrogen storage in materials such as metal hydrides and carbon-based materials offers a way to store hydrogen at low pressures and temperatures, but the technology is still in the early stages of development. Underground hydrogen storage (UHS) has the potential to be a key component of a sustainable energy system, but it requires significant investments in infrastructure and the development of efficient and safe methods of storing and transporting hydrogen.

Researchers extensively studying two types of geological settings for UHS: salt caverns and porous reservoir rocks (including depleted oil/gas fields and aquifers). Currently, the technology for storing hydrogen in salt caverns is in an advanced stage, with four commercial-scale projects worldwide: one in the United Kingdom (Teeside) and three in the United States (Clemens, Moss Bluff, and Spindletop). Salt caverns offer advantages such as fracture prevention due to the plastic behaviour of salt and minimal microbial activity in extreme brine conditions, ensuring the purity of hydrogen. However, their volume is limited compared to aquifers/depleted reservoirs, and operating at greater depths can be challenging due to the rheological properties of salt.

Energy security necessitates large-volume storage solutions, leading researchers to also focus on porous reservoirs. However, there are currently very few pilot projects worldwide to validate their applicability, with examples being the pilot project from RAG Austria and the Hychico project in Argentina. Field-specific hydrodynamical behavior of hydrogen raises concerns, including possible gas losses due to water presence, biological/chemical reactions, and dissolution. Viscous fingering and methanation are widely mentioned in the literature as potential causes of hydrogen loss, emphasizing the need for field-specific observations. Additionally, studying corrosion, steel embrittlement, and hydrogen reactivity with surface facilities is crucial. Cost and public acceptance are significant factors hindering the rapid advancement of the hydrogen economy. Addressing these challenges is essential for the successful integration and widespread adoption of hydrogen as an energy carrier.

Germany, in collaboration with industry partners and research institutions, is prioritizing energy security, emphasizing the development of energy storage sites. There are ongoing projects (published or unpublished) related to salt caverns that are currently in the pilot phase or early development stage. Section 6 (Porous reservoir) includes the distribution of porous reservoirs in Germany, and section 7 describes particularly about the hydrocarbon fields in the northern Upper Rhein Graben. It highlights the old gas and oil fields in Hessen state, such as Stockstadt and Hähnlein, with existing infrastructure and experience from underground gas storage projects. The Stockstadt UGS, developed in an old gas field, has suitable reservoir sands for gas storage, while Hähnlein UGS utilizes aquifer of same stratigraphic formation. Operated by MND Gas Storage Germany GmbH, these facilities have a combined working gas volume of 2.3 TWh. The potential for hydrogen storage in these sites is estimated at 0.8 TWh. The Wolfskehlen

gas field, with similarities to Stockstadt, is also a suitable candidate. Abandoned hydrocarbon fields like Darmstadt, Pfungstadt, and Eich in Rhineland-Palatinate offer additional prospects. Feasibility studies on these fields, backed by recent 3D seismic data and operational information, aim to explore hydrogen storage and in-situ methanation possibilities.

Despite the numerous benefits of hydrogen as an alternative energy source, several challenges remain, including pressure and temperature conditions for transportation, efficiency, behavior of hydrogen in subsurface storage condition, safety, infrastructure, and cost. Nevertheless, worldwide examples of town gas, pure hydrogen storage, and pilot projects are emerging as key players in changing the impact of global warming. To this end, approximately 30 major world economies have issued national hydrogen strategies, with some countries focusing directly on producing green hydrogen from renewable sources and others promising blue hydrogen with CCS or less greenhouse gases from abundant fossil fuels. It is crucial to continue advancing research and development efforts to overcome the challenges associated with hydrogen production and storage, improve efficiency, and cost-effectiveness. With these efforts, the hydrogen economy has the potential to be a game-changer in the transition to a zero-emission future.

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List of Abbreviations and Nomenclature

UHS	Underground hydrogen storage
UGS	Underground gas storage
UMR	Underground methanation reactor
CCS	Carbon capture and storage

Unit conversion

$$1\ \text{bar} = 14.504\ \text{psi} = 100000\ \text{Pa}$$

$$1\ \text{TWh} = 3.6 \times 10^{12}\ \text{kJ}$$

Content

1. Introduction

How to fulfill the energy demand of the world's growing population without jeopardizing the climate? How to reduce green house gas emissions and eventually the effects of global warming? What can be done in the field of Sustainable Energy? How to reduce the dependency of fossil fuels? How efficiently the surplus energy from Renewable sources can be utilized? How to minimize the gap between demand and supply? These few questions have become prominent issues for the existence of Planet Earth, and also motivation for many researchers to work one step closer to the desired solution.

Renewable energy sources like Solar, Wind, Tide have been already proved as alternative energy sources to fossil fuels. But these energy sources are dependent on the weather conditions and the output is fluctuating. However, time to time these sources generate surplus energy and the researchers are working towards storing this in a form of energy source or carrier which can be exploited later to minimize the demand and supply gap.

With this objective, lots of research and pilot projects are running in the domain of power-to-X. Michael Sterner, a professor at OTH Regensburg University in Regensburg, Germany, defines power-to-X as "the means to convert electricity, understood to be primary energy, into an energy carrier, heat, cold, product, or raw material. It is an umbrella term for different ways of generating energy, namely power-to-gas, power-to-liquid, power-to-fuel, power-to-chemicals and power-to-heat[1]." The flow chart in Figure 1 summarizes the power-to-X processes, products and applications. Hydrogen or methane is the final product of power-to-gas (PtG, P-t-G or P2G). This review report is an attempt to have an insight into the state of the art in the field of Hydrogen technology and economics. Most of the important aspects are reported to give an idea the advancement of the technology with subsurface hydrogen storage as the main focus.

The report begins with a common knowledge about the element Hydrogen and general properties essential for further context. The current technologies used for producing hydrogen in large scale is described in the section 4, this section also includes the published occurrences of natural hydrogen. The storage solutions for the produced hydrogen are explained based on its end use and storage period in section 5. As for the sustainability, long-term/large scale storage are under research focus, in section 6 criteria for UHS are summarised from different published and pilot projects. Section 8 gives an overview about the necessary surface facilities required for efficient supply system. Section 9 describes the issues with hydrogen technology, it describes about the physicochemical properties of hydrogen in subsurface conditions which need further research attention, infrastructure advancements and cost factor. World wide examples of different kinds of storage, case studies and feasibility studies are presented in the section 10. Hydrogen strategies by countries and announced national hydrogen projects are mentioned and discussed in section 11 & 12.

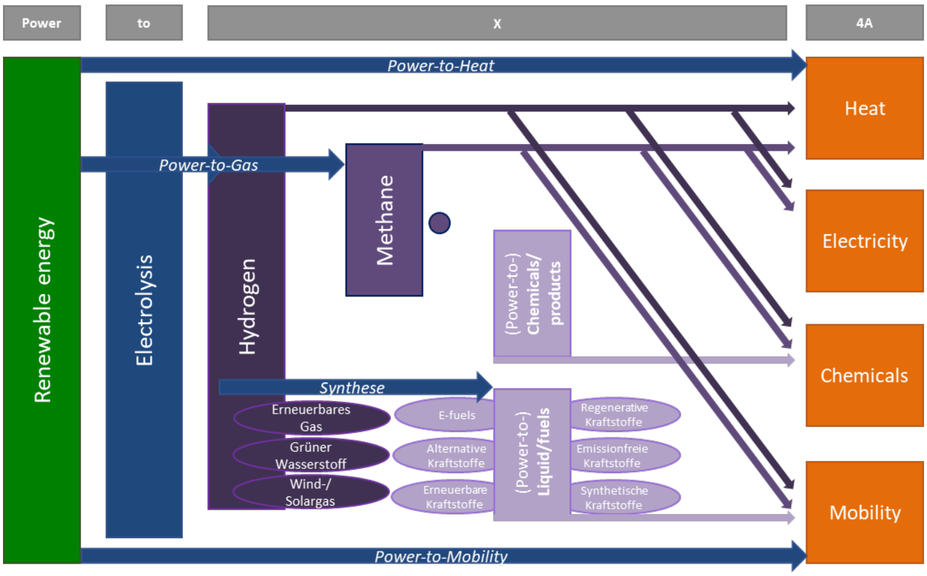


Figure 1: Illustration of power-to-X processes, products and applications[1].

2. Hydrogen: An energy source

As soon as we start our chemistry class in school, we are introduced to the first and lightest element in the periodic table, Hydrogen and its most common and vital compound is H_2O or water. Hydrogen is a chemical element with symbol H and atomic number 1, classified as a nonmetal. Hydrogen is a colorless, odorless and tasteless gas that is both combustible and explosive at room temperature. In 1776, hydrogen was first identified as a distinct element by British scientist Henry Cavendish after he evolved hydrogen gas by reacting zinc metal with hydrochloric acid. In a demonstration to the Royal Society of London, Cavendish applied a spark to hydrogen gas yielding water. This discovery led to his later finding that water (H_2O) is made of hydrogen and oxygen[2]. Later in 1788, French chemist Antoine Lavoisier gave hydrogen its name, which was derived from the Greek words - "hydro" and “genes,” meaning “water” and “born of ”[2]. A report by D. Mendeleev in 1888, mentions about the composition of gas seeping from fractures in coal from a mine near the city of Makiivka, in the Donetsk region of Ukraine. Mendeleev documented that the gas contained 5.8-7.5% hydrogen[3], probably the first documentation of natural hydrogen.

"THE HISTORY OF HYDROGEN" webpage[2] penned by James Jonas, narrates the journey of hydrogen from its discovery, production of hydrogen and oxygen using electrolysis (1800), fuel cell effect (1838), to be used as fuel in rocket propulsion and in 2004 world’s first fuel cell-powered submarine (German navy). Whether hydrogen is an energy source or a carrier/vector, that is a debatable topic and dozens of research works are supporting both terms. Currently researchers and politicians agree that hydrogen is the clean and green fuel option for near future. According to the fourth assessment report (AR4)[4] of Intergovernmental Panel on Climate Change (IPCC), new energy carriers such as hydrogen (section 4.3.4) will only begin to make an impact around 2050, whereas the development of smaller scale decentralized energy systems and micro-grids (section 4.3.8) could occur much sooner (Datta et al., 2002; IEA, 2004d, refer[4] for original citation). Technology issues surrounding energy carriers involve the conversion of primary to secondary energy, transporting the secondary energy, in some cases storing it prior to use, and converting it to useful end-use applications (Figure 2).

It is important to know the definition of energy source and energy carrier/vector, to realise why many researchers consider hydrogen as a carrier/vector rather a source. Energy sources are all solid, liquid and gaseous fuels; electricity; uranium; steam and hot water; and the traditional fuels such as fuelwood, charcoal, vegetal and animal wastes[4]. Energy vectors, aptly described as the human made energy that is not directly usable, but which must be extracted or produced before being transported and stored in appropriate quantities for a prolonged use over time, in applications that are not always calculable in advance[5]. Energy carriers include electricity and heat as well as solid, liquid and gaseous fuels. They occupy intermediate steps in the energy-supply chain between primary sources and end-use applications.

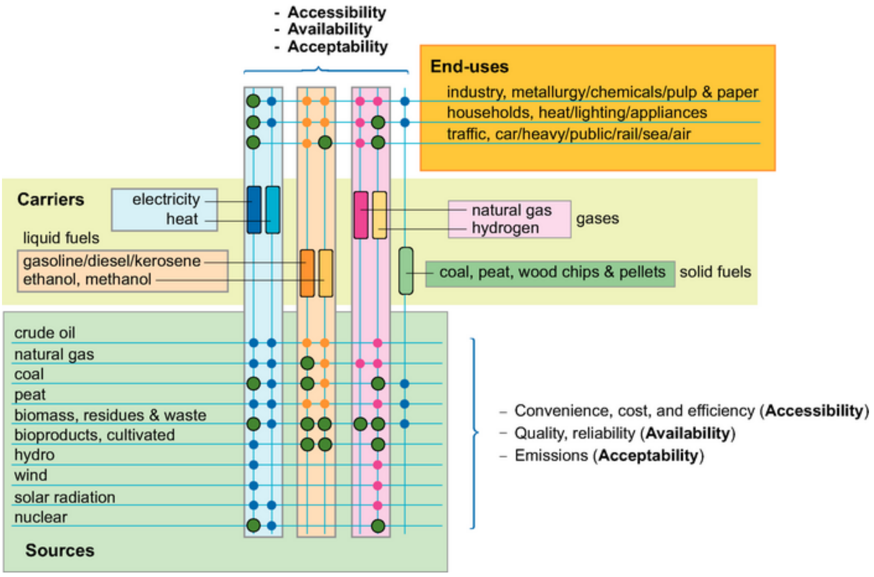


Figure 2: Dynamic interplay between energy sources, energy carriers and energy end-uses[4].

An energy carrier is thus a transmitter of energy[6]. The use of renewable energy resources with integration of energy vectors into the flow chain is pivotal for promoting sustainable energy systems. The cost, volume, energy density and environmental compatibility of alternative energy vectors are of critical importance[5]. Hydrogen is a sustainable alternative to natural gas. Based on the type of primary source used to produce hydrogen, researchers use categorized hydrogen and named it with colour. In literature, articles and on web platform; authors call it sometimes types, colour codes, colour spectrum or kaleidoscope. Table 1 gives an overview of the different kinds of hydrogen based on its initial primary energy sources, the processes involved for the production, by-products and the green house gas footprints.

Panfilov has summarized in his review paper[7] the best way to achieve sustainability would be to store/convert energy from one form to another, and he explained it in regards of hydrogen, which is as follows:

- Electricity conversion to hydrogen: Using low-/high-temperature chemical electrolysis of water to produce hydrogen ($2\,H_2O \longrightarrow 2\,H_2 + O_2$). The electricity can be obtained from renewable energy sources. Standard electrolyzers are used for low-temperature electrolysis. High-temperature electrolysis (800–1200 °C) is conducted in nuclear plants with new generation reactors.
- Hydrogen conversion to electricity: Using pure hydrogen for water synthesis in fuel cells in the presence of a catalyzer ($2\,H_2 + O_2 \longrightarrow 2\,H_2O + 290$ J/mol). The reaction releases electricity as well as heat, the later can be used to cogenerate electricity.
- Hydrogen conversion to methane: reaction of hydrogen with CO_2 or CO at certain condition. This reaction requires catalyzer for initiating the reaction, at higher temperatures ($\sim$ 800 °C) nickel is used. And at lower temperatures ($\sim$ 30–40 °C), the reaction can be initiated in the presence of microorganisms (methanogenic Archaea). This process is also called Sabatier's reaction.

Presently, the main focus is to produce green hydrogen in cost effective and sustainable method.

Table 1: Colour spectrum of hydrogen, summarizing the type of fuel used for production, process, products and green house gas (GHG) footprints.

	Colour	Fuel	Process	Products	GHG
⬛	Brown/Black	Coal	Steam reforming or gasification	$H_2 + CO_2$ (released)	High
⬜	White	N/A	Naturally occurring	H_2	Minimal
▒	Grey	Natural Gas	Steam reforming	$H_2 + CO_2$ (released)	Medium
🟦	Blue		Steam reforming	$H_2 + CO_2$ (% captured and stored)	Low
▨	Turquoise		Pyrolysis	H_2 + C (solid)	Solid carbon (by-product)
🟥	Red	Nuclear Power	Catalytic splitting	H_2 + O2	Minimal
🟪	Purple/Pink	Nuclear Power	Electrolysis		Minimal
🟨	Yellow	Solar Power			Medium
🟩	Green	Renewable Electricity			Minimal

3. Properties of Hydrogen

Physical and chemical properties of hydrogen make it a significant candidate as an energy carrier. For example, it is characterized by a high energy content per mass of 143 MJ/kg, which is around three times higher than for gasoline which means that it can reach a range similar to gasoline and high-pressure vehicles[8]. However, the volumetric energy density of hydrogen gas is 36% of the volumetric energy density of natural gas at the same pressure[9], meaning it requires more storage capacity to deliver energy equivalent to that obtained from hydrocarbons[10]. Burning hydrogen produces water as by-product, qualifying it as zero-emission fuel. In this section, general physical and chemical properties of hydrogen are mentioned which is more of a common knowledge.

3.1. Physical properties[11]

Pure hydrogen is odorless, colorless and tasteless. Hydrogen is a gas at standard conditions. However, at very low temperature and/or high pressures the gas becomes a liquid or a solid. The hydrogen-phase diagram (Figure 3) shows the phase behavior with changes in temperature and pressure. Hydrogen is non-toxic but can act as a simple asphyxiant by displacing the oxygen in the air. Hydrogen has the second lowest boiling point and melting points of all substances, second only to helium. Hydrogen is a liquid below its boiling point of 20 K (–423 °F; –253 °C) and a solid below its melting point of 14 K (–434 °F; –259 °C) and atmospheric pressure. Obviously, these temperatures are extremely low. Temperatures below –100 °F (200 K; –73 °C) are collectively known as cryogenic temperatures, and liquids at these temperatures are known as cryogenic liquids.

Hydrogen has lowest atomic weight of any substance and therefore has very low density both as a gas and a liquid. Vapor density of hydrogen at 20 °C, 1 atm is 0.08376 kg/m^3 and liquid density at normal boiling point, 1 atm is 70.8 kg/m^3. Gaseous hydrogen has a specific gravity of 0.0696 and is thus approximately 7% the density of air (1.203 kg/m^3). Liquid hydrogen has a specific gravity of 0.0708 and is thus approximately (and coincidentally) 7% the density of water. The specific volume of hydrogen gas is 11.9 m^3/kg at 20 °C and 1 atm, and the specific volume of liquid hydrogen is 0.014 m^3/kg at –253 °C) and 1 atm. Vapor density of methane at 20 °C and 1 atm is 0.65 kg/m^3, with a specific volume of approximately 1.5 m^3/kg. This implies that at the given pressure and temperature condition, storing an equal amount of hydrogen (11.9 m^3/kg) would require a volume approximately 8 times larger.

When hydrogen is stored as a liquid, is vaporizes upon expansion to atmospheric conditions with a corresponding increase in volume. When hydrogen is stored as a high-pressure gas at 3600 psi (250 bar) and atmospheric temperature, its expansion ratio to atmospheric pressure is 1:240. Hydrogen molecules are smaller than all other gases, and it can diffuse through many materials considered airtight or impermeable to other gases.

This property makes hydrogen more difficult to contain than other gases. However, the small molecule size that increases the likelihood of a leak also results in very high buoyancy and diffusivity, so leaked hydrogen rises and becomes diluted quickly, especially outdoors. This results in a very localized region of flammability that disperses quickly. The ideal gas relationship can be used accurately to describe the behavior of real gases at pressures up to approximately 1450 psi (100 bar) at normal ambient temperatures. At higher pressures, the results become increasingly inaccurate as illustrated in Figure 4. Hydrogen is commonly stored as a high-pressure gas at up to 3600 or even 5000 psi (250 to 350 bar) at ambient temperatures. Therefore, the ideal gas relationship cannot be used accurately at gas storage pressures. When used as vehicle fuel, the low density of hydrogen necessitates that a large volume of hydrogen be carried to provide an adequate driving range. To evaluate the efficiency of a fuel, it is necessary to consider the energy content and the energy density of the kind. Energy content is the amount of heat produced by the burning of 1 gram of a substance, and is measured in joules per gram (J/g).

The energy content of a fuel can be determined by burning an amount of the fuel, capturing the heat released in a known mass of water in a calorimeter and quantifying by a fuel's higher heating value (HHV) known as gross calorific value and lower heating value (LHV) known as net calorific value. The amount of energy (in Btu or Joules) for a given volume (in ft^3 or m^3) of fuel is known as energy density. Thus, energy density is the product of the energy content (LHV) and the density of a given fuel. Energy density is further explained in two terms: volumetric energy density (VD) and gravimetric energy density (GD). The gravimetric energy density (GD) of an element shows how much energy per kilogram or gram can be stored, while its volumetric energy density (VD) shows how much energy per litre can be stored. Table 2 summarises the heating values of other fuels in comparison to hydrogen. From the comparison, it can be inferred that hydrogen is a strong candidate when considering GD, as it has twice the gravimetric energy density compared to methane. However, hydrogen falls behind methane in terms of VD, as it has only one-third of the VD of methane (Table 2).

Hydrogen is flammable over a very wide range of concentrations in air (4–75%) and it is explosive over a wide range of concentrations (15–59%) at standard atmospheric temperature. The flammability limits increase with temperature as illustrated in Figure 5.

Hydrogen has an octane rating greater than 130, and is higher than any other fuel. While hydrogen is highly combustible, it does not tend to spontaneously ignite under high pressure. Hydrogen burns with a pale blue flame that is nearly invisible in daylight. The flame may appear yellow if there are impurities in the air like dust or sodium. A pure hydrogen flame will not produce smoke. Hydrogen flames are readily visible in the dark or subdued light. A hydrogen fire can be indirectly visible by way of emanating “heat ripples” and thermal radiation, particularly from large fires.

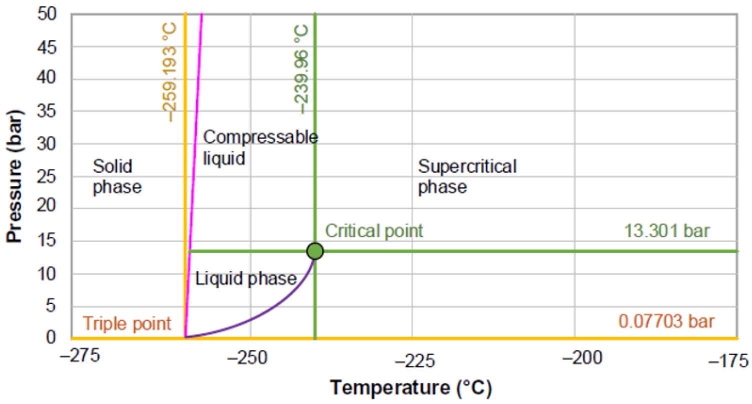


Figure 3: Hydrogen phase diagram.

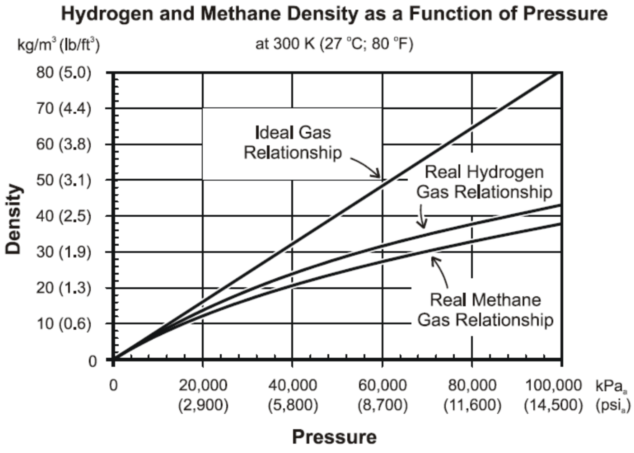


Figure 4: Behaviour of hydrogen and methane due to pressure change.

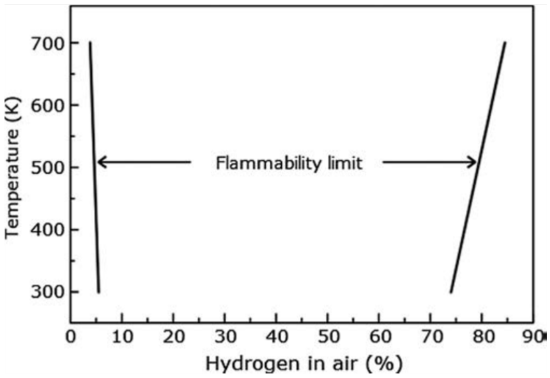


Figure 5: Effect of temperature on flammability limits of hydrogen in air (pressure 100kPa).

Table 2: Heating Values of Comparative Fuels.

Fuel	Higher Heating Value	Lower Heating Value	Energy Density (LHV)
Hydrogen	141.86 kJ/g	119.93 kJ/g	10,050 kJ/m^3; gas at 1 atm and 60 °F (15 °C) 1,825,000 kJ/m^3; gas at 3000 psi (200 bar) and 60 °F (15 °C) 4,500,000 kJ/m^3; gas at 10000 psi (690 bar and 60 °F (15 °C) 8,491,000 kJ/m^3; liquid
Methane	55.53 kJ/g	50.02 kJ/g	32,560 kJ/m^3; gas at 1 atm and 60 °F (15 °C) 6,860,300 kJ/m^3; gas at 3000 psi (200 bar) and 60 °F (15 °C) 20,920,400 kJ/m^3; liquid
Propane	50.36 kJ/g	45.6 kJ/g	86,670 kJ/m^3; gas at 1 atm and 60 °F (15 °C) 23,488,800 kJ/m^3; liquid
Gasoline	47.5 kJ/g	44.5 kJ/g	31,150,000 kJ/m^3; liquid
Diesel	44.8 kJ/g	42.5 kJ/g	31,435,800 kJ/m^3 minimum; liquid
Methanol	19.96 kJ/g	18.05 kJ/g	15,800,100 kJ/m^3; liquid

*The Higher and Lower Heating Values are at 25 °C and 1 atm. 1 kJ/m^3 = 0.0268392 BTU/ft^3

3.2. Chemical properties[12][13]

Hydrogen is a chemical element located in subgroup A of the first group, and in subgroup A of the seventh group in the first period. As its outer level only contains 1 electron, hydrogen has both oxidative and reductive properties. If it surrenders its electron, hydrogen is left with a free orbital, which can form chemical bonds according to a donor-acceptor mechanism. One molecule of hydrogen dissociates into two atoms ($H_2 \longrightarrow 2\,H$) when energy equals to or is greater than the dissociation energy (i.e., the amount of energy required to break the bond that holds together the atoms in the molecule) is supplied.

The dissociation energy of molecular hydrogen is 104,000 cal/mol, written as 104 kcal/mol. Atomic hydrogen is very reactive. It combines with most elements to form hydrides (e.g., sodium hydride, NaH), and it reduces metallic oxides, a reaction that produces the metal in its elemental state. The surfaces of metals that do not combine with hydrogen to form stable hydrides (e.g., platinum) catalyze the recombination of hydrogen atoms to form hydrogen molecules and are thereby heated to incandescence by the energy that this reaction releases. Molecular hydrogen can react with many elements and compounds, but at room temperature, the reaction rates are usually so low as to be negligible. This apparent inertness is in part related to the very high dissociation energy of the molecule. At elevated temperatures, however, the reaction rates are high.

The redox potential of hydrogen (H_2) is 0 volts at standard conditions (25 °C, 1 atmosphere pressure, pH 7), which means that hydrogen gas is an excellent reference electrode for measuring the redox potential of other substances. In aqueous solutions, the redox potential of hydrogen is affected by changes in pH. As the pH of the solution increases (i.e., becomes more basic), the concentration of hydrogen ions (H^+) decreases, and the redox potential of hydrogen becomes more negative. Conversely, as the pH decreases (i.e., becomes more acidic), the concentration of hydrogen ions increases, and the redox potential of hydrogen becomes more positive. This pH dependence of the redox potential of hydrogen is due to the fact that the oxidation and reduction reactions of hydrogen involve the transfer of protons (H^+ ions) and electrons (e^-) simultaneously. Therefore, changes in pH can affect the availability of these reactants and alter the equilibrium between the oxidized and reduced forms of hydrogen. The redox potential of hydrogen is pH-dependent in aqueous solutions, and its value changes with the concentration of hydrogen ions.

Sparks or certain radiations can cause a mixture of hydrogen and chlorine to react explosively to yield hydrogen chloride, as represented by the equation $H_2 + Cl_2 \longrightarrow 2\,HCl$. Mixtures of hydrogen and oxygen react at a measurable rate only above 300 °C, according to the equation $2\,H_2 + O_2 \longrightarrow 2\,H_2O$. Such mixtures containing 4%–94% hydrogen ignite when heated to 550–600 °C or when brought into contact with a catalyst, spark, or flame. The explosion of a 2:1 mixture of hydrogen and oxygen is especially violent. Almost all metals and nonmetals react with hydrogen at high temperatures. At elevated temperatures and pressures, hydrogen reduces the oxides of most metals and many metallic salts to the metals. For example, hydrogen gas and ferrous oxide react, yielding metallic iron and water, $H_2 + FeO \longrightarrow Fe + H_2O$; hydrogen gas reduces palladium chloride to form a palladium metal and hydrogen chloride, $H_2 + PdCl_2 \longrightarrow Pd + 2\,HCl$.

Hydrogen is absorbed at high temperatures by many transition metals; and metals of the actinoid and lanthanoid series to form hard, alloy-like hydrides. These are often called interstitial hydrides because, in many cases, the metallic crystal lattice merely expands to accommodate the dissolved hydrogen without any other change. In interstitial or metallic hydrides hydrogen dissolves in a metal to form non-stoichiometric compounds (solid solutions) of formula MH_n. They possess the typical metallic properties of luster, hardness, and conductivity and are called interstitial hydrides because the hydrogen occupies interstices in a FCC, HCP, or BCC metal lattice. The process of interstitial hydride formation is reversible and metals can dissolve varying amounts of hydrogen depending on the number of interstices available. Because of this interstitial hydrides have been considered as storage materials for hydrogen (refer Section 5.1).

Hydrogen can be stored by reacting it with some organic compound. For example, hydrogen can be stored as cyclohexane by combining it with benzene, which can be dissociated into benzene and hydrogen when required. Physicochemical properties of hydrogen at subsurface conditions discussed elaborately in the Section 9. The section describes the behaviour of hydrogen at subsurface conditions such as solubility, diffusion, subsurface reactions with formation fluids and rocks and microbial activities.

4. Generation of Hydrogen

Free hydrogen is rare in the nature. However, there are evidences and case studies by some researchers which ensures that it is not impossible. The occurrence of natural hydrogen will be discuss in the second part of this section. Nevertheless, hydrogen is mainly produced artificially on an industrial scale. Methods part of this section summarizes the various methods used. Figure 6 illustrates different existing methods for producing hydrogen from fossil fuels and renewable sources. Shiva Kumar & Himabindu compiled in their review paper[14] for hydrogen production, the methods, its advantages and disadvantages, efficiency and cost, shown in Table 3.

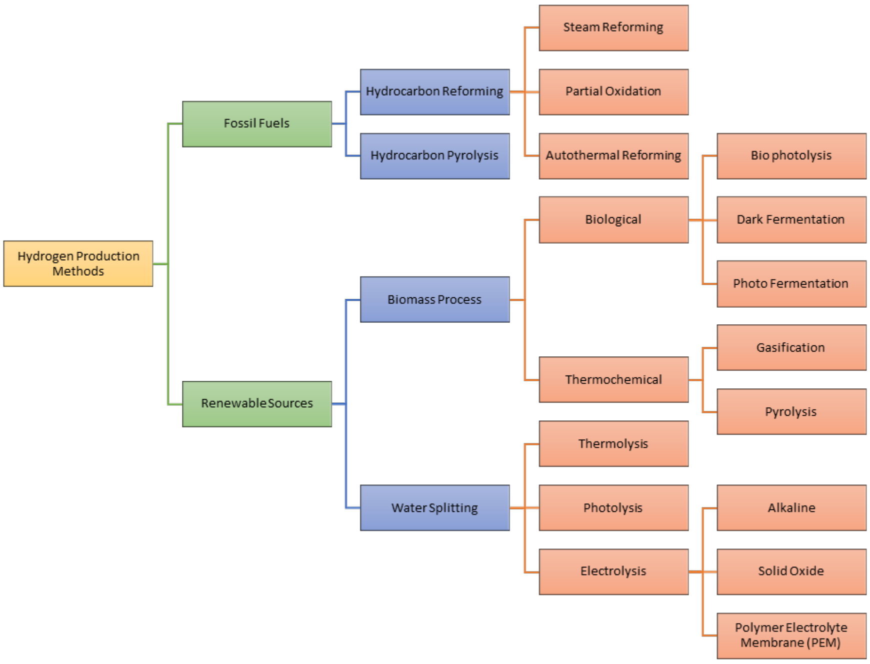


Figure 6: Various Hydrogen Production Methods[14].

Table 3: Various Hydrogen production methods along with their advantages, disadvantages, efficiency and cost (refer[14] for original citation).

Hydrogen production Method	Advantages	Disadvantages	Efficiency	Cost [$/kg]
Steam Reforming	Developed technology & Existing infrastructure.	Produced CO, CO_2 Unstable supply.	74–85	2.27
Partial Oxidation	Established technology.	Along with H_2 Production, produced heavy oils and petroleum coke.	60–75	1.48
Auto thermal Reforming	Well established technology & Existing infrastructure.	Produced CO_2 as a byproduct, use of fossil fuels.	60–75	1.48
Hydrocarbon Pyrolysis	CO_2 neutral.	Carbon black or Tar formation.	–	1.59–3.2
Bio photolysis	Consumed CO_2, Produced O_2 as a byproduct, working under mild conditions.	Low yields of H_2, sunlight needed, large reactor required, O_2 sensitivity, high cost of material.	10–11	2.13
Dark Fermentation	Simple method, H_2 produced without light, no limitation O_2, CO_2-neutral, involves to waste recycling.	Fatty acids elimination, low yields of H_2, low efficiency, necessity of huge volume of reactor.	60–80	2.57
Photo Fermentation	Involves to waste water recycling, used different organic waste waters, CO_2-neutral.	low efficiency, Low H_2 production rate, sunlight required, necessity of huge volume of reactor, O_2-sensitivity.	0.1	2.83
Gasification	Abundant, cheap feedstock and neutral CO_2.	Fluctuating H_2 yields because of feedstock impurities, seasonal availability and formation of tar.	30–40	1.77–2.05
Pyrolysis	Abundant, cheap feedstock and CO_2-neutral.	Tar formation, fluctuating H_2 amount because of feedstock impurities and seasonal availability.	35–50	1.59–1.70
Thermolysis	Clean and sustainable, O_2-byproduct, copious feedstock.	High capital costs, Elements toxicity, corrosion problems.	20–45	7.98–8.40
Photolysis	O2 as byproduct, abundant feedstock, No emissions.	Low efficiency, non-effective photocatalytic material, Requires sunlight.	0.06	8–10
Electrolysis	Established technology Zero emission Existing infrastructure O_2 as byproduct.	Storage and Transportation problem.	60–80	10.30

4.1. Methods[14]–[17]

In this section, the processes for production are explained, which are currently used world wide for industrial scale production of hydrogen. This includes some significant methods such as different kinds of electrolysis, which are gaining popularity for the production of green hydrogen.

Hydrogen generation from fossil fuel

- Hydrogen from natural gas methane-steam reforming (Figure 7): Grey hydrogen is produced from the steam reformation of methane. It is a thermal process, where at first the methane is desulfurized and fed into the reformer. Then the high temperature (700–1000°C) steam reacts with the methane under 3–5 bar pressure, generates syngas (H_2 + CO). It is an endothermic process. The next step is the reaction between the generated CO with steam, to produce CO_2 and additional H_2 , called water gas shift reaction. It is an exothermic process, generating small amount of heat. At the final stage, the impurities and by-products are eliminated and hydrogen is collected. Ethanol, propanol and gasoline can be also used for steam reformation.

- Hydrogen from hydrocarbon partial oxidation: This process can be used to generate hydrogen from most of the hydrocarbon based fossil fuels such as natural gas, coal and heavy oil. Partial oxidation of coal is also known as coal gasification. Partial oxidation can be done using a catalyst at around 590°C and also without a catalyst in the temperature range of 150–1315°C. Noncatalytic partial oxidation is ideal for hydrogen generation from heavy hydrocarbons that cannot react over catalyst instantly. Similar to methane-steam reforming process, syngas is generated in the first step. The hydrocarbon is oxidised with limited supply of oxygen for generating syngas. If the oxidization is performed with air instead of pure oxygen, as byproduct nitrogen, small amount of carbon dioxide, and other components can be generated. The "water gas shift" reaction and hydrogen purification stages are similar to methane-steam reforming process.

- Hydrogen from coal gasification (Figure 8): This process is adopted by Kopper–Totzek, thus named as Kopper–Totzek (K–T) gasifier. In this process, the crushed coal is partially oxidized by steam and oxygen at atmospheric pressure in the K-T gasifier. The oxygen is extracted by the air separation process. The raw gas produced in the gasifier is then cooled and quenched with water to remove the ash particles from the raw gas. The purified gas called as syngas, which is then passed through the compression chamber, water-gas shift conversion chamber, and finally purification chamber. Hydrogen is collected at about 2.8 MPa (400 psi) pressure and of purity greater than 97.5%.

- Autothermal reforming: The autothermal reforming is the combined state of the partial oxidation and the steam-reforming processes. The autothermal term defines the heat exchange between endothermic steam reforming and exothermic partial oxidation reactions. The hydrocarbons are reacted in a “thermo reactor” with the catalyst and oxygen + steam. The process takes place in the regions of combustion ($\sim$ 1900°C) and conversion ($\sim$ 900 C–1100°C).

$$\mathrm{CH_4 + O_2 \longrightarrow CO + 2\,H_2}$$

- Thermal cracking: Hydrocarbon compounds are broken down in the presence of a catalyst by being heated in an oxygen-free environment and at very high temperatures, hydrogen and carbon are obtained. Since this reaction is endothermic, 10% of the natural gas feed is used for the energy input requirement. Thermal cracking does not have greenhouse gas emissions. If the hydrocarbon is methane, the reaction takes place as follows:

$$\mathrm{CH_4 \longrightarrow C + 2\,H_2}\ (\Delta H = 75.6\,\mathrm{kJ/mol})$$

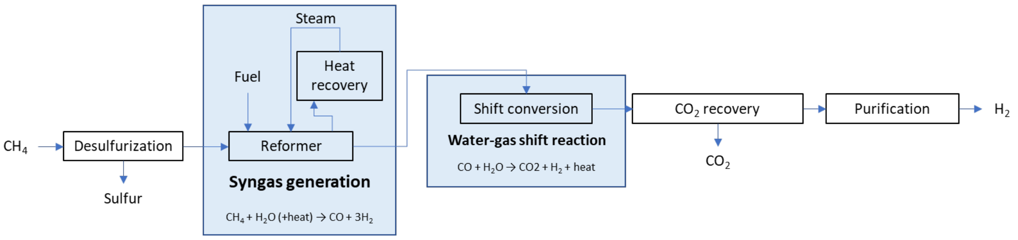


Figure 7: Flow diagram of methane-steam reforming[15],[16].

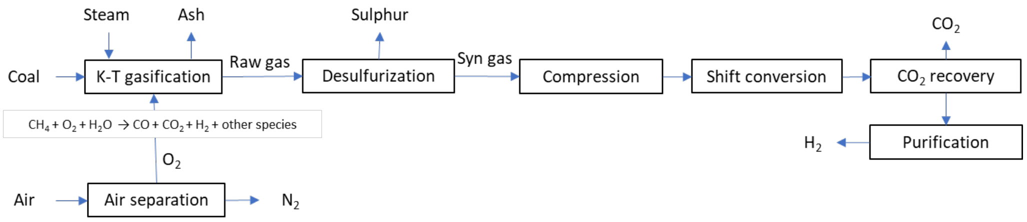


Figure 8: Flow diagram of Kopper–Totzek coal gasification for hydrogen generation[15],[16].

Hydrogen generation from water:

- Electrolysis: The basic concept is to perform electrolysis of water to produce hydrogen and oxygen ($2\,H_2O \longrightarrow 2\,H_2 + O_2$). The reaction, however, is very endothermic thus the required energy input is provided by electricity. A typical electrolysis unit or electrolyzer consists of a cathode and an anode immersed in an electrolyte, and generally when electrical current is applied water splits and hydrogen is produced at the cathode ($H_2O + 2\,e^- \longrightarrow H_2 + O^{2-}$)while oxygen is evolved on the anode side ($O^{2-} \longrightarrow \frac{1}{2}\,O_2 + 2\,e^-$). Three types of electrolysis technologies are popular for hydrogen generation: i) Alkaline water electrolysis, ii) Polymer electrolyte membrane (PEM) electrolysis iii) Solid oxide electrolysis (SOEC).

  Alkaline electrolysis operates at lower temperatures such as 30–80 °C with aqueous solution (KOH / NaOH) as the electrolyte, the concentration of the electrolyte is 20% to 30%. In alkaline water electrolysis process, asbestos diaphragm and nickel materials are used as the electrodes. The diaphragm having in the middle of the cell and it is separates the cathode and anode also separates the produced gases from their respective electrodes and avoiding the mixing of produced gases electrolysis process.

  PEM water electrolysis technology is similar to the PEM fuel cell technology, where solid polysulfonated membranes (Nafion®, fumapem®) was used as a electrolyte (proton conductor). PEM water electrolysis has great advantages such as compact design, high current density (above 2 A/cm^2), high efficiency, fast response, small footprint, operates under lower temperatures (20–80 °C) and produced ultra pure hydrogen and also produced oxygen as a by-product.

  Solid oxide electrolysis operates at high pressure and high temperatures 500–850 °C and utilizes the water in the form of steam. Solid oxide electrolysis process conventionally uses the O^{2-} conductors which are mostly from nickel/yttria stabilized zirconia. ZrO_2 doped with 8 mol% Y_2O_3 is used as the electrolyte, which at high temperatures is highly conductive for oxygen ions (charge carrier), and has good thermal and chemical stability.

- Thermolysis: Thermal cracking of the water at high temperature produces hydrogen and oxygen ($H_2O + \text{heat} \longrightarrow aH_2O + bH_2 + cO_2$). In this method, when the temperature is raised to 1400°C or higher, the vapor molecules break down gradually into hydrogen and oxygen. The temperature should be raised to 2500–3000°C to produce hydrogen in a way that meets industrial use.

Some researchers showed concern to the idea of water usage for electrolysis due to the water scarcity problems across the world. Some researches are made viable using sea water for electrolysis. However, this remains a questionable topic for the economic efficiency and foremost for sustainability. Figure 9 shows the predicted water consumption in 2050 for different sectors worldwide, agriculture remaining the most high consuming sector and hydrogen production would be about 1/100th portion of agriculture.

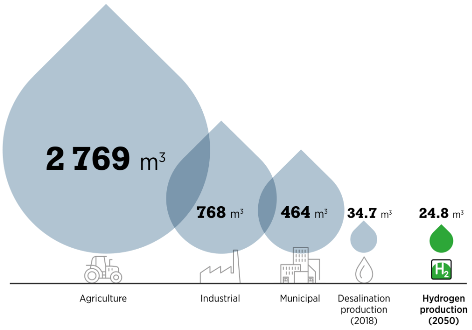


Figure 9: Water consumption of hydrogen in 2050 compared with selected sectors today (billion cubic metres)[18].

4.2. Natural Hydrogen

70 Metric Ton of hydrogen are consumed each year worldwide, mainly for industrial purposes. This hydrogen, called 'grey hydrogen', is manufactured by steam reforming of hydrocarbons (78%) and coal (18%). 'Green hydrogen', produced by electrolysis of water, represents only 4% of this mix. These methods are not environment-friendly as CO_2 is a by-product. However, hydrogen also exists in the subsoil, in its natural state[19], it is called 'white hydrogen' or 'native hydrogen'[20].

The review paper by Zgonnik[3], elaborately mentions about the current status of natural hydrogen exploration worldwide. The author tries to fill the gap in data by reviewing all the reported cases from the Eastern and Western countries. In his review, he mentions about the earliest mentions of natural hydrogen, e.g. in an 1888 report by D. Mendeleev on the composition of gas seeping from fractures in coal from a mine near the city of Makiivka, in the Donetsk region of Ukraine. Mendeleev documented that the gas contained 5.8–7.5% hydrogen.

Hydrogen emanations have been reported in three geological tectonic settings by many researchers: i) extension zones (Mid Oceanic Ridge, Iceland, and African Rift); ii) compression zones involving ophiolitic nappes (Oman, Philippines, New Caledonia); and iii) stable intracratonic basins above Archean to Proterozoic basement[21]. Though the knowledge regarding natural hydrogen is still in a very premature stage, researchers states following three possible origin of natural hydrogen: i) H_2 may come from water/rock interaction in the crust. Within this case, the origin of H_2 is the water. The H_2O reduction and the release of H_2 could be caused by the oxidation of mineral rich rocks such as olivine, or by the radiolysis induced by the natural radioactivity of rocks such as granite; ii) H_2 may be generated by bacterial/algae activity near the surface; and finally; and iii) H_2 may come from a deep source and corresponds to the primordial H_2 of the solar system.

Known active H_2 systems and continuous H_2 seepage at the Earth's surface are characterized by the occurrence of bright, large scale "fairy circles"[22]. Several circular depressions have been described in Russia, in Mali and in the United States. Some authors reported by analysing satellite images that these topographical depressions may appear or disappear in some years time span. Figure 10 shows an areal photograph of fairy circle in Brazil taken by the R & D group ENGIE Brasil Energia, the monitoring set up can be also seen in the photograph[22]. Some authors repeatedly mentioned about the natural occurrence of hydrogen in Bourakebougou (Mali). Specifically Prinzhofer et al.[22],[23] mentioned about the discovery; and the production is active for the past 4 years without any substantial decrease in the wellhead pressure indicating a continuous influx to the reservoir.

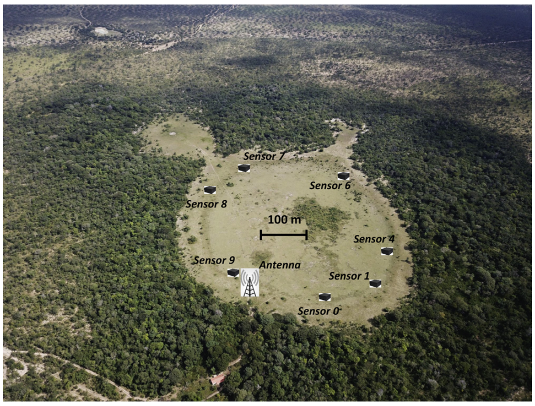


Figure 10: Photo of the location of H_2 monitoring in a circular depression of the São Francisco Basin (Brazil)[22]

It was a accidental discovery of hydrogen with a purity of 98% while drilling for water resources. Later in 2012, a Canadian company Petroma (now Hydroma) began exploration, and drilled 24 wells. The occurrence of hydrogen in the formation is related to the existence of multiple layers of dolerite beds and aquifers[24]. The global distribution of natural hydrogen emissions is shown in the Figure 11. They appear along oceanic ridges, on obducted oceanic plates (ophiolites from Oman, New Caledonia, the Philippines, Turkey, etc.) or in mountain ranges (Pyrenees). They are also observed on the edges of graben (Rhine Graben and Rhine Ditch also known as Lower Rhine Embayment) and in Proterozoic cratons (Russia, USA, Brazil, Australia, Africa, etc.)[20]. Recently Tian et al.[24] reported the worldwide activities and its nature in the review paper, Figure 12 shows the distribution of hydrogen detected according to different settings.

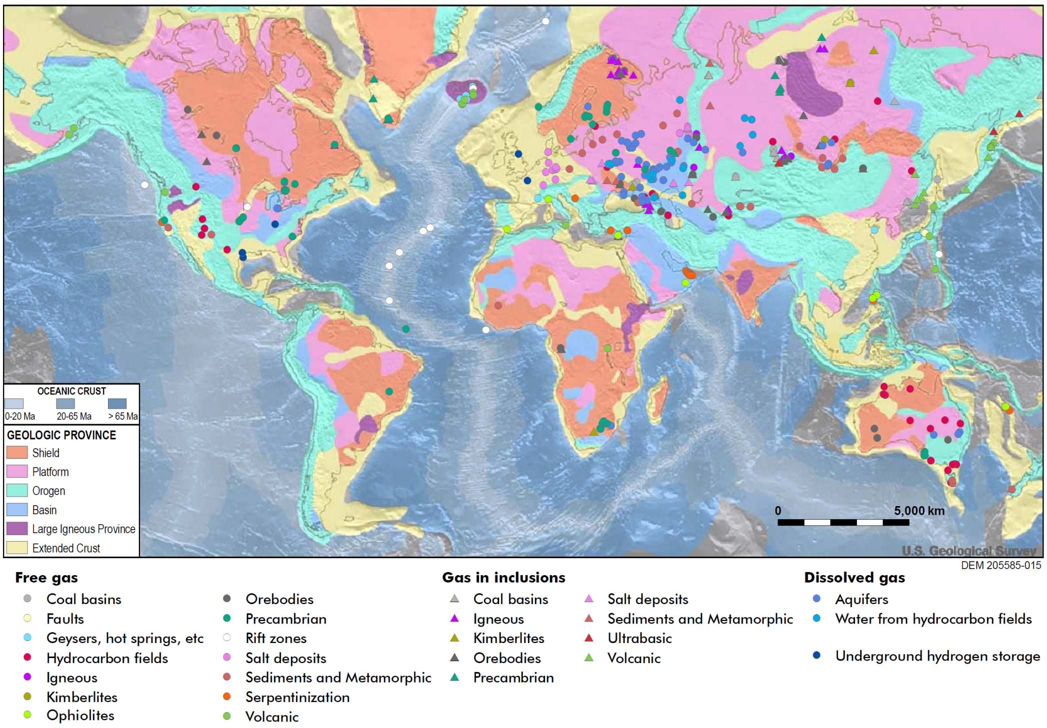


Figure 11: Locations and geological environments of recorded hydrogen measured at >10% volume around the world. As noted by Zgonnik (2020), the relatively dense distribution of hydrogen discoveries across Europe and Asia reflects biases in data collection rather than an accurate indication of the local prospectivity for molecular hydrogen. (refer to[25] for original citation, modified from Zgonnik 2020; Truche et al. 2020, Truche and Barzakina 2019; Boreham et al. 2021a; Sherwood Lollar et al. 2014; Warr et al. 2019; Moretti et al. 2021.)

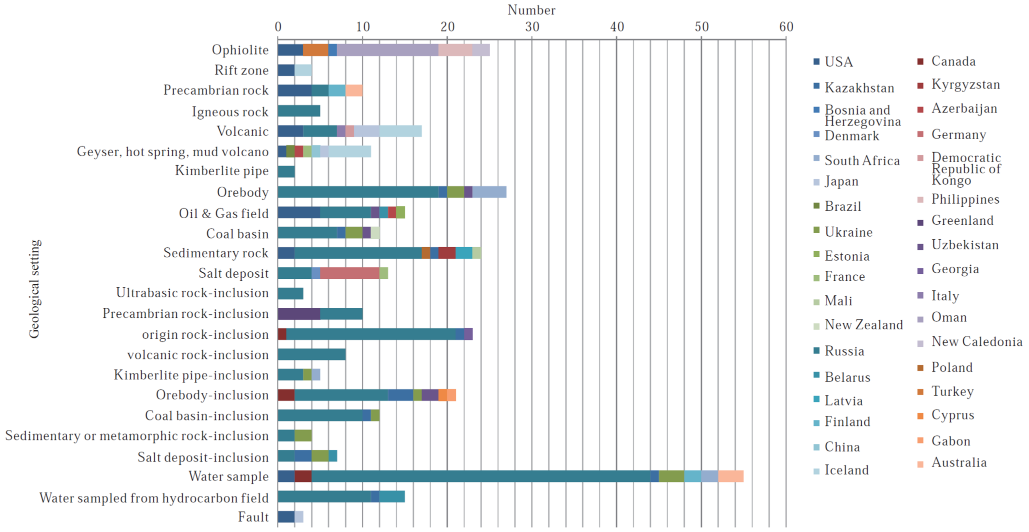


Figure 12: Distribution of hydrogen detected according to different settings[24]

5. Storage infrastructures

Several probable methods exist for the hydrogen storage: compressed gas tanks, cryogenic compressed liquid hydrogen tanks, metal hydride storage, physical storage, and underground storage (e.g. salt caverns). The unstable pressure, continuous leakage of gas, and expensive insulation, make cryogenic liquid hydrogen storage a poor choice for PtG applications.

Underground storages are cheapest options, but these storages are good for high capacity and long term storage. These are not viable options for PtG systems, which require small scale, onsite, and temporary hydrogen storage[17]. In this section, different kinds of storage options were described based on the need such as capacity, ease of transportation, duration and type of gases.

5.1. Small scale storage/Short term storage

Züttel in his 2004 review paper[9] explained, how hydrogen is currently stored in small scale for industrial uses. He reported in detail six storage methods and phenomena:

- High-pressure gas cylinders (up to 800 bar): High-pressure gas cylinders with a maximum pressure of 20 MPa are commonly used storage system. There are lightweight composite cylinders which are able to withstand a pressure up to 80 MPa, enabling to reach volumetric density of 36 kg/m^3 (ca. half of liquid H_2 at normal boiling point). Hydrogen can be compressed using standard piston type mechanical compressors.

- Liquid hydrogen in cryogenic tanks (at 21 K): Due to the low critical temperature of hydrogen (33 K), liquid hydrogen can only be stored in open systems, because there is no liquid phase existing above the critical temperature. The pressure in a closed storage system at room temperature could increase to about 104 bar. The volumetric density of liquid hydrogen is 70.8 kg/m^3 and slightly higher than that of solid hydrogen (70.6 kg/m^3). The challenges of liquid hydrogen storage are the energy-efficient liquefaction process and the thermal insulation of the cryogenic storage vessel in order to reduce the boil-off of hydrogen.

  The simplest liquefaction cycle is the Joule–Thompson cycle (Linde cycle). The gas is first compressed, and then cooled in a heat exchanger, before it passes through a throttle valve where it undergoes an isenthalpic Joule–Thomson expansion, producing some liquid. The cooled gas is separated from the liquid and returned to the compressor via the heat exchanger (Flynn 1992). Hydrogen, however, warms upon expansion at room temperature. In order for hydrogen to cool upon expansion, its temperature must be below its inversion temperature of 202 K. Therefore, hydrogen is usually pre-cooled using liquid nitrogen (78 K) before the first expansion step occurs. The boil-off rate of hydrogen from a liquid hydrogen storage vessel due to heat leaks is a function of the size, shape and thermal insulation of the vessel.

- Physisorption of hydrogen on materials with a large specific surface area (at T<100 K): The origin of the physisorption of gas molecules on the surface of a solid are resonant fluctuations of the charge distributions and are therefore called dispersive interactions or Van der Waals interactions. In the physisorption process, a gas molecule interacts with several atoms at the surface of the solid. Physisorption of hydrogen on carbon nanostructures are vastly studied and reported. Along with it, hydrogen absorption of zeolites of different pore architecture and composition were also analysed in different temperature and pressure conditions. The big advantages of the physisorption for hydrogen storage are the low operating pressure, the relatively low cost of the materials involved, and the simple design of the storage system. The rather small amount of adsorbed hydrogen on carbon, together with the low temperatures necessary, are significant drawbacks of hydrogen storage based on physisorption.

- Metal hydrides, H_2 absorbed on interstitial sites in a host metal (at ambient pressure and temperature): Hydrogen reacts at elevated temperature with many transition metals and their alloys to form hydrides. The electropositive elements are the most reactive, i.e. scandium, yttrium, the lanthanides, the actinides, and the members of the titanium and vanadium groups. The binary hydrides of the transition metals are predominantly metallic in character and are usually referred to as metallic hydrides. They are good conductors of electricity, possess a metallic or graphite-like appearance, and can often be wetted by mercury. The lattice structure is that of a typical metal with atoms of hydrogen on the interstitial sites; for this reason they are also called interstitial hydrides. One of the most interesting features of the metallic hydrides is the extremely high volumetric density of the hydrogen atoms present in the host lattice. Metallic hydrides reach a volumetric hydrogen density of 115 kg/m^3 e.g. LaNi5. Most metallic hydrides absorb hydrogen up to a hydrogen to metal ratio of H/M=2.

- Complex hydrides, H_2 chemically bonded in covalent and ionic compounds (at ambient pressure): The group one, two and three light elements (e.g. Li, Mg, B, Al) build a large variety of metal–hydrogen complexes. They are especially interesting because of their light weight and the number of hydrogen atoms per metal atom, which is in many cases 2. The main difference of the complex hydrides to the above-described metallic hydrides is the transition to an ionic or covalent compound of the metals upon hydrogen absorption. Hydrides with a hydrogen to metal ratio of >2 are ionic or covalent compounds and belong to the complex hydrides. Greater ratios up to H/M=4.5, e.g. BaReH9 (Yvon 1998, refer[9] for original citation), have been found.

- Through oxidation of reactive metals, e.g. Li, Na, Mg, Al, Zn with water: Hydrogen can be generated from metals and chemical compounds reacting with water. The major challenge with this storage method is the reversibility and the control of the thermal reduction process in order to produce the metal in a solar furnace. Another indirect way of using hydrogen are complex hydrides dissolved in water as a fuel. Borohydrides in alkaline media are potential fuels for fuel cells due to their high energy and power density.

The efficiency of storage is usually measured by two parameters: the gravimetric density, (GD), namely the weight percentage of hydrogen stored of the total weight of the system (hydrogen+container), and the volumetric density, (VD), that is the stored hydrogen mass per unit volume of the system. Both parameters are important, since for practical application a hydrogen storage device must be both light and compact[26]. In Figure 13, Edwards et al.[27] reports the gravimetric and volumetric densities of various hydrogen storages.

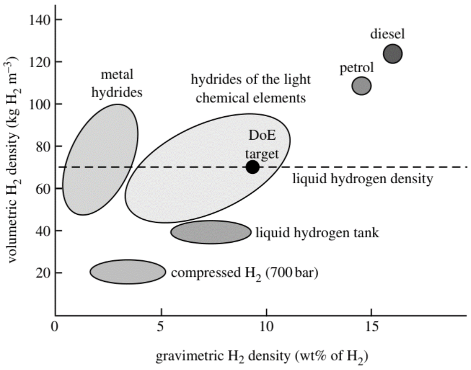


Figure 13: Gravimetric and volumetric densities of various hydrogen storage options (note: weight and volume of the storage container are included). 'DoE target' represents the US Department of Energy target for 2015 set for an 'ideal' hydrogen storage material. Metal hydrides are conventional, heavy metal hydrides such as LaNi5, etc[27].

The article states that It is becoming increasingly accepted that solid-state hydrogen storage using ionic–covalent hydrides of light elements, such as lithium, boron, sodium, magnesium and aluminium (or some combination of these elements), represents the only method enabling one to achieve the necessary gravimetric and volumetric target densities. For transportation use, a suitable solid-state storage material should be able to store a high weight per cent and a high volume density of hydrogen and rapidly absorb and desorb hydrogen at–or close to–room temperature and pressure. Ideally, such a material should be made from cheap materials using a low-energy preparation method, be resistant to poisoning by trace impurities, have a good thermal conductivity in charged and uncharged conditions, be safe and reusable on exposure to air and have the ability to be regenerated and be readily recycled. This clearly represents a particularly challenging set of credentials for the ideal storage material; at present, no single material meets all of these requirements[27].

5.2. Large scale storage/Long term storage

A considerate amount of researches or milestones have been established for replacing fossil fuels and natural gas with hydrogen. Hydrogen is also considered to be an energy carrier which can eliminate the seasonal fluctuations of renewable energy. Due to its high energy potential, hydrogen is capable of replacing up to 60% of the natural gas used for non-industrial activities[28]. However, the biggest concern remains the amount of hydrogen required to replace the necessity in every sector. There are some known examples across the world, where hydrogen has been stored with other gases or in pure form in geological reservoirs based on the experience of storing natural gas underground. These geological reservoirs are named as UHS.

According to researches, this could be a economical solution to store large amount of hydrogen, to regulate the energy supply and demand, energy price regulation and offer industries hydrogen backup supply[7]. Majorly, four types of geological reservoirs as UHS are discussed in literature: 1) Salt caverns, 2) Aquifers 3) Depleted oil and gas reservoirs and 4) Hard rock caverns. Some researchers also mention about abandoned mines as an additional option used in some parts of the world to store natural gas. Małachowska et al.[8] summarised the general characteristics, advantages, disadvantages and utilization of the potential large scale UHS, shown in Table 4.

Table 4: Comparison of potential UHS reservoirs (modified after Małachowska et al.[8]).

Geological Formation	General	Advantages	Disadvantages	Utilization
Salt caverns	Artificial underground cavities in salt domes or salt layers, created by controlled injection of fresh water and leaching of salt.	Plastic properties of salt protect caverns against the appearance and spreading of fractures and the loss of impermeability. In rare situation bacteria can thrive in highly concentrated brine–Pure H_2 can be stored (no loss of H_2 due to transformation into other gases).	Restricted cavern volume compared to an aquifer/depleted reservoir. Due to the rheological property of salt (salt deformation due to increased pressure and temperature), stability is difficult to maintain with greater depths.	Salt caverns in UK and USA for storing Pure hydrogen.
Aquifers	Porous and permeable rock formations (typically sandstones or carbonate rocks), containing fresh or saline water.	Availability–common in all sedimentary basins, often located near energy consumers such as large cities. High capacity.	Geological structure usually unknown—considerable investment costs, time-consuming exploration works. Possible gas losses due to the presence of water, biological and chemical reactions.	Natural gas and carbon dioxide storage (Belgium, Denmark, Norway, France, and Germany), when neither depleted gas, oil fields nor caverns are available.
Depleted gas and oil fields	Permeable sandstones or carbonate rocks.	The existence of surface and subsurface infrastructure. Geological structure usually well known–lower investment costs. The gas remained in depleted gas fields can serve as a cushion gas.	The presence of hydrocarbon residues in oil fields reduces hydrogen purity. The possibility of chemical reactions (e.g., conversion of hydrogen to methane) and hydrogen dissolution in the oil–losses of hydrogen.	Natural gas storage.
Abandoned mines	Reservoirs after excavation of deposits.	Existing infrastructure. Plenty of abandoned mines in various types of geological formations across the Europe.	Designed and constructed with the intention of natural resources extraction not storage of a gas–safety problems.	Only rare examples of abandoned mines conversion into gas storage are known. Natural gas storage in Belgium, USA, and Germany (closed now due to high cost associated with the sealing of the shafts).
Hard rock caverns	Massive, homogenous rocks (e.g., metamorphic crystalline rocks such as granite and gneiss) with minimal structural or textural weaknesses, great mechanical stability, and low permeability.	Lined rock caverns have suitable parameters for gas storage.	Necessity of additional sealing provided by groundwater management or lining of the host rock–additional investment costs.	Liquid hydrocarbons storage in Europe (mostly in Scandinavia because of favorable geological structures) since 1950s. The natural gas cavern in Czech Republic (Háje) and Sweden (Skallen).

5.3. Types of gas

Panfilov[7] wrote about four types of UHS based on the form of energy initially produced, the form of the final energy consumed, the methods of energy conversion, and the combination between these elements. He explained that to store pure hydrogen which is later used in fuel cells, the chemical transformation of hydrogen during storage should be prohibited. In contrast, if the aim is to use the hydrogen for gas-fired turbines or to inject it into natural gas pipeline, the enrichment of the stored gas by methane or other energy carriers is probably welcome.

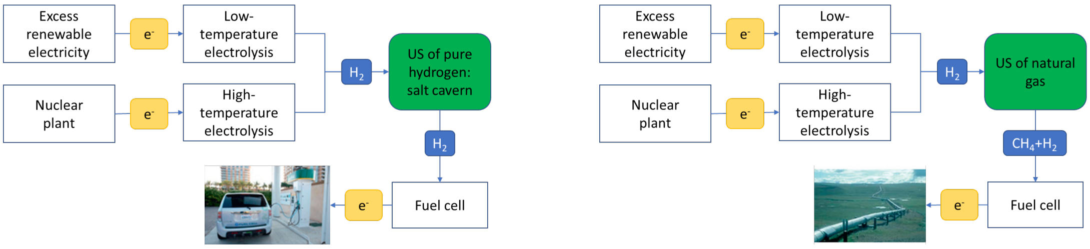
- Underground storage of pure hydrogen: This hydrogen is meant to be used in fuel cells where it will converted to electricity for vehicles. Salt caverns are the best choice to store ultra-pure hydrogen.

- Underground storage of a mixture with natural gas lean in hydrogen: Pure hydrogen from water electrolysis is injected into an underground natural gas storage in small amounts (6–15%). The small quantity of H_2 assures that the energy potential of the stored gas is not reduced significantly and avoids damage of the existing infrastructure (embrittlement). The gas is used as fuel. The blended H_2 and CH_4 can also be separated after storage, to obtain pure hydrogen.

- Underground storage of rich hydrogen mixture with CO, CH_4, and CO_2 (syngas or town gas): Syngas is the mixture of H_2 (20–40%) and CO and he mixture of H_2 (50–60%), CO, and CH_4 is called town gas. Both can be stored in an aquifer, depleted gas reservoir, or salt cavern. The stored gas can be utilised in two forms: as electricity obtained from thermo-mechanical conversion in gas turbines and as fuel (town gas) for lighting and heating without any conversion.

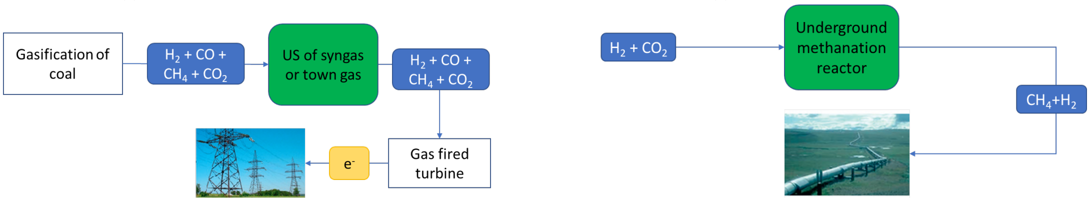
- Underground methanation reactor (UMR): The mixture of H_2 and CO_2 in an aquifer or depleted gas reservoir can be converted into methane by methanogenic bacteria initiate the Sabatier's methanation reaction. The process can be initiated by the bacteria at low temperatures. The resulting gas is injected into the grid of natural gas and used as fuel.

The review paper by Liebscher et al.[29] illustrates a compiled map (Figure 15) of Europe showing the distribution of sedimentary basins and salt deposits which can be explored for underground gas storage. Some of them are already under research stages for pilot projects. The map is presented in this report for the illustrating the ongoing research efforts for UHS.



(a) Underground storage of pure H_2.

(b) Lean H_2 blended with natural gas.



(c) Rich H_2 blend with CO and CO_2.

(d) Underground methanation reactor (UMR).

Figure 14: Energy cycle of four principle types of UHS[7].

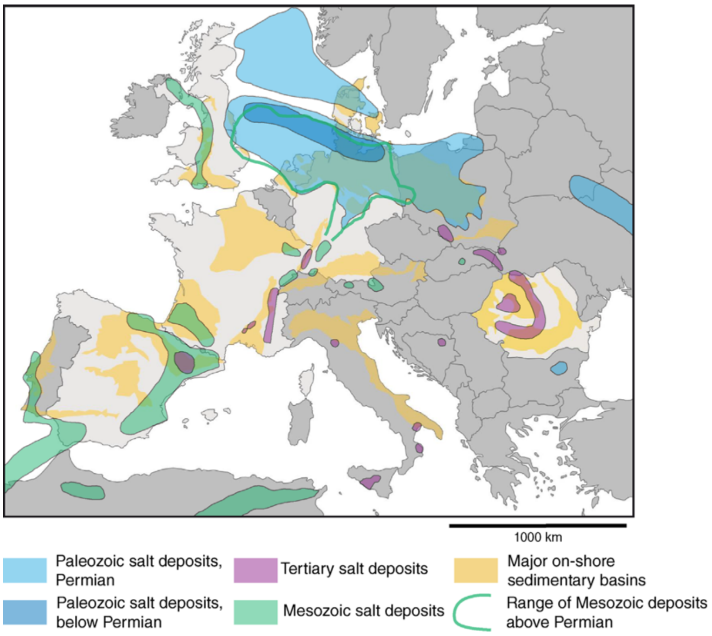


Figure 15: Geographic distribution of major on-shore sedimentary basins and salt deposits in Europe, that potentially provide geologic settings for hydrogen storage in saline aquifers, depleted gas/oil reservoirs, and salt caverns. Modified and compiled by Libescher et al.[29] after HyUnder Assessment Report (2013).

5.4. Hydrogen liquid carrier: Ammonia

In current research fields and literature, a lot of researchers are working towards the direction of storing hydrogen in other forms such as ammonia and methanol. Aziz et al.[30] reviewed the current state of art for storing hydrogen in form of ammonia. The review paper covers several potential technologies, in current conditions and in the future, for ammonia production, storage and utilization. Table 5 shows the property comparison between other popular hydrogen derivative and ammonia. The comparison brings out the conclusion that liquid ammonia is much easier to store with respect to hydrogen due to higher density and other physical properties. Methanol can become a competitor, however the synthesis, utilization and decomposition process of methanol release CO_2[30].

Table 5: Characteristics comparison of compressed hydrogen, liquid hydrogen, methanol and liquid ammonia (refer Aziz et al.[30] for original reference).

Properties	Unit	Compressed Hydrogen	Liquid Hydrogen	Methanol	Liquid Ammonia
Storage method	-	Compression	Liquefaction	Ambient	Liquefaction
Temperature	°C	25 (room)	-252.9	25 (room)	25 (room)
Storage pressure	MPa	69	0.1	0.1	0.99
Density	kg/m3	39	70.8	792	600
Explosive limit in air	%vol	4–75	4–75	6.7–36	15–28
Gravimetric energy density (LHV)	MJ/kg	120	120	20.1	18.6
Volumetric energy density (LHV)	MJ/L	4.5	8.49	15.8	12.7
Gravimetric hydrogen content	wt%	100	100	12.5	17.8
Volumetric hydrogen content	kg-H2/m3	42.2	70.8	99	121
Hydrogen release	-	Pressure release	Evaporation	Catalytic decomposition T >200 ◦C	Catalytic decomposition T >400 ◦C
Energy to extract hydrogen	kJ/mol-H2	-	0.907	16.3	30.6

Ammonia can be produced mainly by three conversion technologies: Haber–Bosch, electrochemical and thermochemical cycle processes. Haber-Bosch process has been invented by Fritz Haber and Carl Bosch about 100 years ago and well developed in comparison to other two. The ammonia synthesis occurs according to the reaction $3\,\mathrm{H_2} + \mathrm{N_2} \rightleftharpoons 2\,\mathrm{NH_3}$ ($\Delta H^{\circ}{}_{27\,^{\circ}\mathrm{C}} = -46.35\,\mathrm{kJ/mol}$). The production of ammonia from natural gas is conducted by reacting methane (natural gas) with steam and air, coupled with the subsequent removal of water and CO_2. The products of this process are hydrogen and nitrogen, which are the feedstock for the main ammonia synthesis (Figure 16)[30]. Liquid ammonia can be stored in pressurised spheres (20 °C, 10 bar), semi-cryogenic spheres (0 °C, 4 bar) and large capacity cryogenic tanks (-33 °C). Londe mentions in his Geostock article[31] about possibility of storing ammonia underground where salt is not available. Ammonia could be stored in hard rock caverns in almost any kind of rock providing that it is strong enough to be excavated without heavy support. However, the underground storage of ammonia is not straightforward, as ammonia has a high affinity with water and the dissolution of ammonia in water is highly exothermic (2000 kJ/kg of ammonia). Consequently, ammonia needs to be isolated from water. In hard rock caverns, this would require the use of a steel liner (Figure 17).

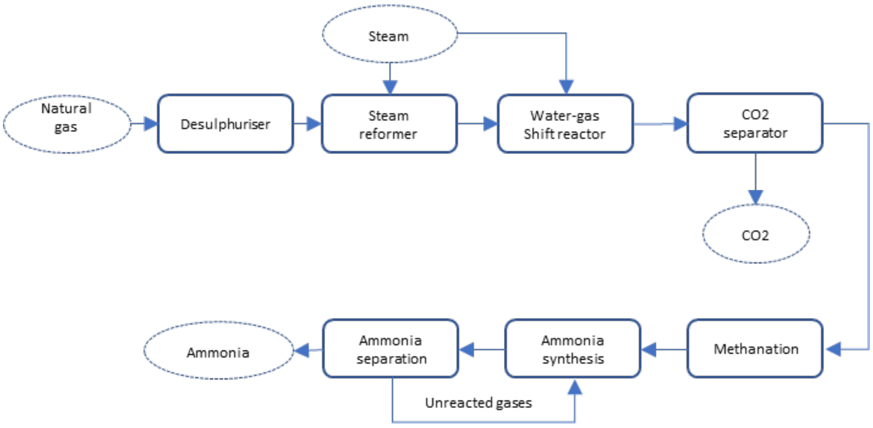


Figure 16: Schematic diagram of ammonia production from natural gas, employing the Haber–Bosch process[30].

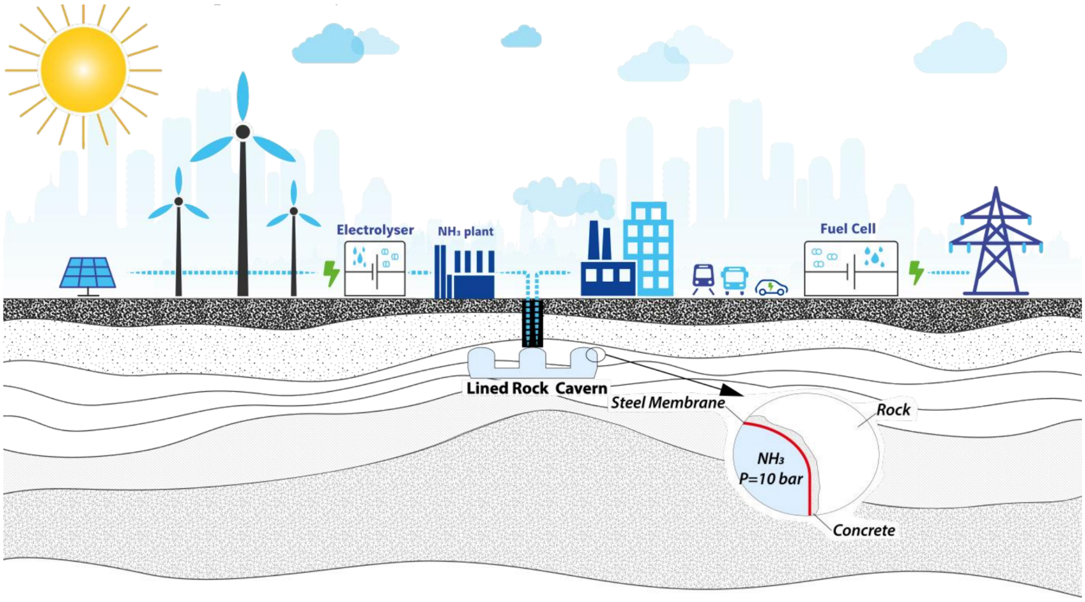


Figure 17: Lined Rock Cavern for ammonia storage[31].

6. Criteria for UHS

It is now common knowledge that the criteria used for selecting underground gas storage for natural gas can be utilized for developing hydrogen storage. However, one to one technological transformation from natural gas storage to hydrogen storage is not possible. The physicochemical properties of hydrogen are different with respect to natural gas and carbon dioxide, and the behaviour of hydrogen in subsurface requires further research attention.

However, some important aspects are known from lab experiments, data from depleted gas reservoirs, town gas or syn gas storages and pure hydrogen gas storage. Depleted gas reservoirs qualify the requirement of confinement and operability criteria because of already existing data and infrastructure. In case of aquifers, the structure, the mobility of water and the seal remain significant criteria. In case of salt caverns, the sealing is provided by the impermeable host rock.

A number of factors limit the maximum depth and pressure desirable for underground storage, including the costs of drilling wells or sinking shafts, the cost of compression, and the geothermal gradient, because high storage temperatures partially offset the volumetric efficiency gained by greater pressure[32]. Except in the case of depleted fields and aquifers, the higher cost of exploration at greater depth also is a limiting factor, whereas the depth of storage caverns in salt is limited by the rheological properties of salt[32]. Hydrogen being low-density gas (0.089 kg/m^3 at 0°C and at 1 atm pressure), is difficult to store. One kilogram of H_2 occupies 11 m^3, which makes it necessary to compress or liquefy it in order to operate and store it at reasonable mass or energy densities[33]. As the storage pressure increases, less volume is required for a given quantity of stored gas. The greater the pressure, the more gas that can be stored in a given volume. For purposes of approximation of storage capacity, the ideal gas law is generally sufficient; the supercompressibility of natural gas also slightly favors storage pressures below 2000 psi (137.8951 bar)[32].

Geological reservoirs are the only way to store such large amounts of hydrogen. These exist in the form of salt caverns or porous media, i.e., aquifers or depleted natural gas reservoirs. In addition, they guarantee security due to the absence of contact with atmospheric oxygen (a mixture of hydrogen and oxygen is explosive at practically any concentration)[7]. These underground facilities have significant advantages over surface facilities in terms of gas storage, including increased safety, lower costs, better space management, and the wide availability of suitable geological structures[33].

6.1. Porous reservoir

Bouteldja et al.[34] listed eight main criteria for selecting and scoring depleted reservoirs and aquifers for conversion to UHS and suggest to target reservoirs having a net thickness ranging between 3 and 100 meters, a minimum area of 0.3 km^2 and maximum of 60 km^2 and a maximum top depth of 2500 m.

- Preferably good reservoir thicknesses,
- A well-delineated structure with sizeable closure height,
- Efficiency of the sealing overburden formation (which might be challenging to assess and prove for an aquifer),
- Good and well-connected porosities and high permeabilities for each reservoir zone,
- A "tank type" production mechanism (influence of cushion gas), even though in some cases a uniform water-drive may be advantageous (pressure support),
- A depth allowing for a pressure range adequate for supply at grid pressure,
- Formation fluids with low impact on storage gas quality and unlikely to result in corrosion issues (sweet gas, low salinity formation water, etc.).
- Additionally, a well-documented exploration and production history is expected for depleted fields.

The authors specified some guiding magnitudes related to the reservoir property for the selection process (refer the Table 1. in the report[34]). The scoring and screening criteria were decided based on roughly the characteristics of 564 underground gas storage facilities in porous media in operation in the world (6 in aquifers and 488 in depleted hydrocarbon fields).

Table 6 and Figure 18 show the characteristics and location of the H2STORE research sites in Germany. The reservoirs were predominantly clastic reservoirs.

The characteristics from the mentioned reservoirs can be considered as a starting point for preliminary screening of any geological reservoir.

Table 6: Overview of the H2STORE research areas (Figure 18) and their geological/structural variations in reservoir setting[35].

	(1) Bavaria	(2) Brandenburg	(3) Lower Saxony	(4) Thuringia	(5) Saxony-Anhalt
Age	~25 Ma	~225 Ma	~250 Ma	~250 Ma	~270 Ma
Stratigraphy	Tertiary	Keuper	Early-Middle Buntsandstein	Early-Middle Buntsandstein	Rotliegend
Current depths	~1600 m	~650 m	~1700 m	~800 m	~3500 m
Current temperature	~53-60 °C	~40 °C	~55-122 °C	~40-80 °C	~125 °C
Facies	molasses (turbidites & debris flow]	fluviatile, shallow marine	playa platform	playa platform, fluviatile	playa platform
Lithology	heterogeneous (sand- & mudstone, carbonate clasts)	heterogeneous (sand-, silt- & mudstone)	heterogeneous (ooid-, silt-, sand- & mudstone)	silt- & sandstone	silt- & sandstone
Reservoir type	gas storage site	CO_2 storage site	gas storage site	depleted gas reservoir	depleted gas reservoir
Overburden	shallow marine limestone & clastic sediments	massive mudstone & carbonate	marine shale, sulphate, halite	marine shale, sulphate, halite	salt & carbonate

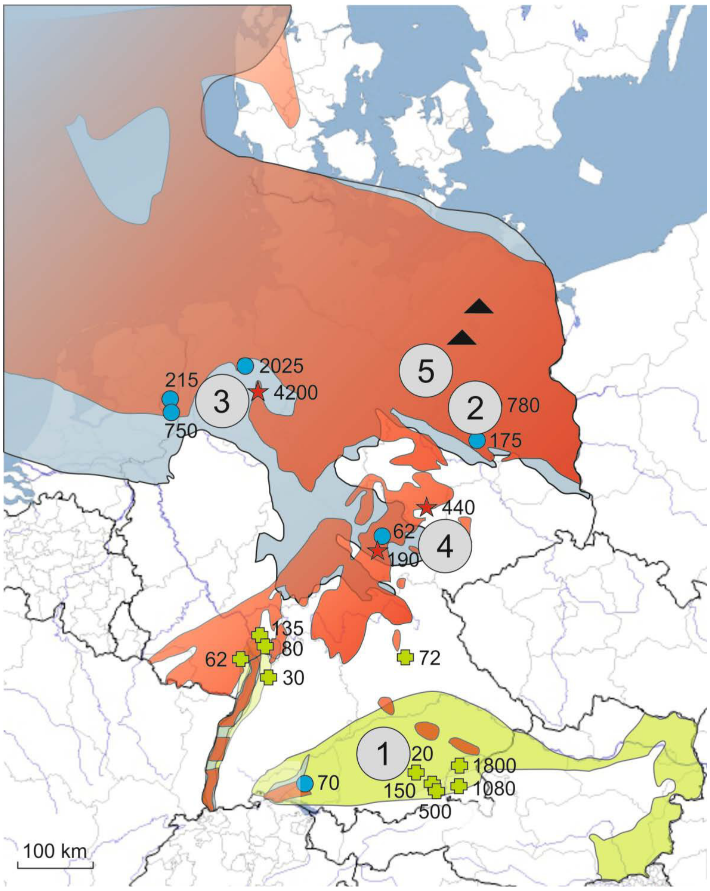


Figure 18: Storage reservoir and research sites (No. 1-5, cf. Tab. 1) of the H2STORE project in Germany. In red = Permo-Carboniferous, in light blue = Early Triassic and in green = Tertiary strata. Symbols mark storage reservoirs in use (red stars, blue dots, green crosses) and under construction (black triangles). Numbers refer to storage capacities in Mio. m^3[35].

6.2. Salt caverns

Małachowska et al.[8] studied the potential of salt caverns in Poland for subsurface hydrogen storage. They compared their simulated cavern with prospective salt caverns across the world. Table 7 summarises the characteristics of the prospective salt caverns. Below 6000 ft (1828.8 m) salt deformation is great due to increased pressure and temperature, and stability is difficult to maintain even for well-engineered and constructed caverns[36]. The size of the caverns depends on the thickness of the salt seams, but also on their porosity and permeability, which should be as low as possible to fulfill the storage function, otherwise, the gas from the reservoir could leak into the surrounding layers, causing costly hydrogen losses. Caverns typically have a capacity of about 30,000 m^3 to over 700,000 m^3. The temperature in the caverns varies from about 40 to less than 260 °C. The pressure conditions in caverns range from 4 to 24 MPa, although are mostly around 10 MPa[8]. Figure 19 illustrates the different shapes and depth of salt caverns across the world, compiled by Małachowska et al.[8].

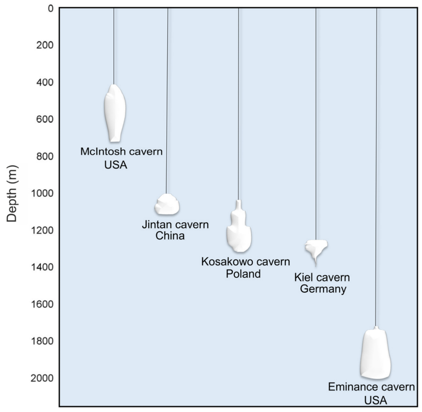


Figure 19: Examples of different shapes of salt caverns across the world[8].

Table 7: Characteristics of prospective hydrogen salt caverns[8]

Location	Dimensions	Capacity (m^3)	Geology	Pressure Conditions (MPa)	Additional Information
Simulated cavern	Thickness: min 30 m; depth: 30 m.	565000	Salt formation density 2200 kg/m^3; salt formation specific heat 840 J/kgK; thermal conductivity 5.24 W/mK.		High porosity and permeability.
Germany	Thickness: 280 m; height * diameter: 150 * 20 m.	300000	Precambrian to Quaternary salt rocks (layers of 400–2000 m).	4.6–7.2	Heat condition: >100 °C, lack of water, high porosity and permeability.
UK (Chesire salt basin–NW England)	Thickness: 250 m; depth: 600–1200 m; height * diameter: 60–80 * 80–100 m.	100000–300000	Various proportions of halite, anhydrite, gypsum, K-Mg minerals and other minerals. Minerals occur as an admixture in rock salt beds: anhydrite, gypsum, carnallite, kainite, langbeinite, bischofite, polyhalite, sylvite, kieserite, clay, minerals, quartz. Salt layer: 400/500–2000 m.		Low porosity and permeability.
SW Poland	Thickness: 150–1800 m; depth: 1000–2000 m.	730800	Upper Permian salt deposits.	7.4–23.8	Good viscoplastic behaviour, low porosity and permeability, lack of water.
Rogozno Poland	Thickness. max 196.3 m; height * diameter: 300 * 49 m	32000	Clay-sulphate (gypsum—anhydrite).	8–10	
Lubien Poland	Thickness: max 893 m		Sulphate (gypsum-anhydrite)	8–10	
China	Depth: 750–1250 m	200000	The cavern section—argillaceous rock salt and mudstone interlayers (glauberite mudstone, anhydrite mudstone, clay shales, silty mudstone).	6–16	Low porosity and permeability.
China, Jiangsu province, Jitan salt mine	Depth: 900–1100m, height * diameter: 85 * 73 m	210000	Cretaceous to Tertiary lacustrine bedded salt rocks. Caprock and interlayer including: glauberite, gypsum, anhydrite, siltstone.		Very low porosity and permeability. In situ vertical stress of 21–25 Mpa.

6.3. Criteria for Underground methanation reactor (UMR)

The Hychico-BRGM Pilot Project[37] focuses on the potential of depleted gas reservoirs to accomplish methane production by biological processes. The pilot project takes account of its distance from the hydrogen plant, size, depth, original pressure, geological and mechanical conditions among others. The goal is to find out the factors that could lead to the production of methane by means of hydrogen and CO_2, including the identification of different types of microorganisms that can be involved in such metabolic reactions. The selected reservoir belongs to the glauconitic type, a deposit of marine origin in the developed Golfo de San Jorge Basin in Argentine Patagonia. The technical and reservoir parameters of the storage site are summarised in Table 8.

Table 8: UHS and its influencing parameters for methanation.

Reserve properties	
Type of reserve	Glauconitic. Clay-covered sandstone
Depth (m)	815
Original pressure (bar)	26.5
Original gas volume (Nm^3)	750,000
Average thickness (m)	2.5
Porosity (%)	25
Absolute permeability (mD)	500
H_2O saturation (%)	55
Temperature (°C)	55

7. Gas and oil fields in Hessen state, Germany

The German government, in collaboration with industry partners, research institutes, and universities, is strongly emphasizing the need to accelerate efforts in the direction of energy security, with a particular focus on energy storage sites. The report highlights various research projects from Germany, offering valuable insights into this endeavor. Figure 18 illustrates the distribution of porous reservoirs mapped across Germany at different stratigraphic levels under H2STORE project. The map also includess the locations of storage reservoirs in the northern Upper Rhein Graben (southern part of Hessen State), marked with green crosses. This specific section of the report describes the old gas and oil fields located in the Hessen state (Figure 21 and 20). These fields were discovered during the mid-20th century in the northern part of the Upper Rhine Graben. Over the years, hydrocarbons were extracted from different stratigraphic levels in these fields. What makes these fields particularly attractive for UHS is the existing infrastructure and extensive experience gained from Underground gas storage (UGS) projects like Stockstadt, Hähnlein, and Frankenthal.

Stockstadt UGS facility is situated in the northern part of the Upper Rhine Graben and was originally an old gas field. As described in the excursion report by Plein[38], it is characterized by an anticlinal structure bounded by faults with different orientations. The structure has an approximate thickness of 40 meters, and its top is encountered at a depth of 360 meters below mean sea level. The reservoirs used in the Stockstadt UGS are two unconsolidated sands of Tertiary age, known as Jungtertiar II. These reservoir sands include Sand 7, which has a thickness of 5 meters, and Sand 8, with a thickness of 15 meters. These two sands are separated by a 25-meter thick clay bed. The depths of Sand 7 and Sand 8 are 400 meters and 360 meters below mean sea level, respectively. Importantly, Sand 8 is hydraulically connected to the nearby Hähnlein UGS. The average porosity of the reservoir sands in the Stockstadt UGS is 0.35, and the permeability is above 1 Darcy, making them suitable for gas storage purposes. On the other hand, the Hähnlein UGS, located nearby, is developed in an aquifer, which implies that it utilizes porous rock formations as a storage medium for gas.

BEB Erdgas Erdöl GmbH originally developed the Stockstadt UGS facility, which has been in operation since 1963. In late 1985, it became the property of Ruhrgas AG. Since 2016, MND Gas Storage Germany GmbH has been operating both the Hähnlein and Stockstadt UGS facilities. Combined, these facilities have a working gas volume (CH_4) of approximately 2.3 terawatt-hours (TWh), which is equivalent to 235.4 million cubic meters (m^3) of gas. Notably, the Stockstadt UGS accounts for approximately 60% of the total storage volume of both facilities. If we consider storing H_2 in these two sites, it would yield approximately 0.8 TWh. To provide a sense of scale, as mentioned in Pfeiffer et al.[39], the electricity consumed in Schleswig-Holstein (a state in northern Germany) for the year 2011 was 42.82×10^6 GJ ($\sim$ 11.89 TWh). Therefore, the week-long energy demand for the entire state of Schleswig-Holstein would be 0.82×10^6 GJ ($\sim$ 0.227 TWh).

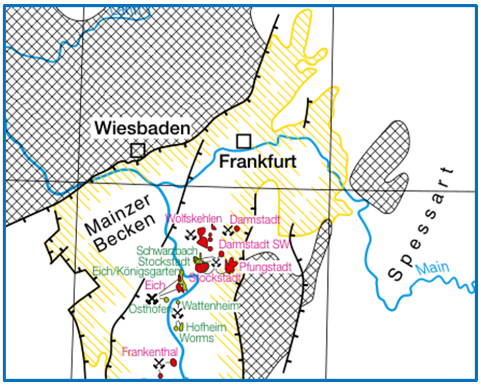


Figure 20: Inset map showing the locations of the hydrocarbon fields in the state of Hessen.

Wolfskehlen gas field is located 6.8 kilometers south of the Stockstadt structure and is structurally related to it. It also has similar reservoir dimensions as Stockstadt and Hähnlein. Both fields have produced gas from the Upper Tertiary I sands. The geological, stratigraphic, and tectonic features of the Wolfskehlen gas field are well-documented in a report written by Dr. E. W. Straub, a geologist at Gewerkschaft Elwerath[40]. At the Wolfskehlen horst structure, the top of the reservoir (Upper Tertiary I) is encountered at depths approximately between 350 to 365 meters below Mean Sea Level (MSL), while the base of the reservoir is found around depths of 420 to 450 meters below MSL. Reservoir properties are similar to the Stockstadt reservoir sands. There are a few more abandoned hydrocarbon fields such as Darmstadt, Pfungstadt, and Eich (Rhineland-Palatinate).

In recent years, there has been extensive coverage of this area through the acquisition of 3D seismic data for identifying new prospects. Additionally, operational data for the Underground gas storage (UGS) is accessible upon request. Conducting feasibility studies on these fields is of great interest as it can explore the possibilities of hydrogen storage, in-situ methanation, and potential pilot projects in the near future. These fields meet the necessary criteria, such as suitable geological settings, existing infrastructure, and the availability of relevant data, making them promising candidates for further exploration and development in the context of energy storage and hydrogen utilization.

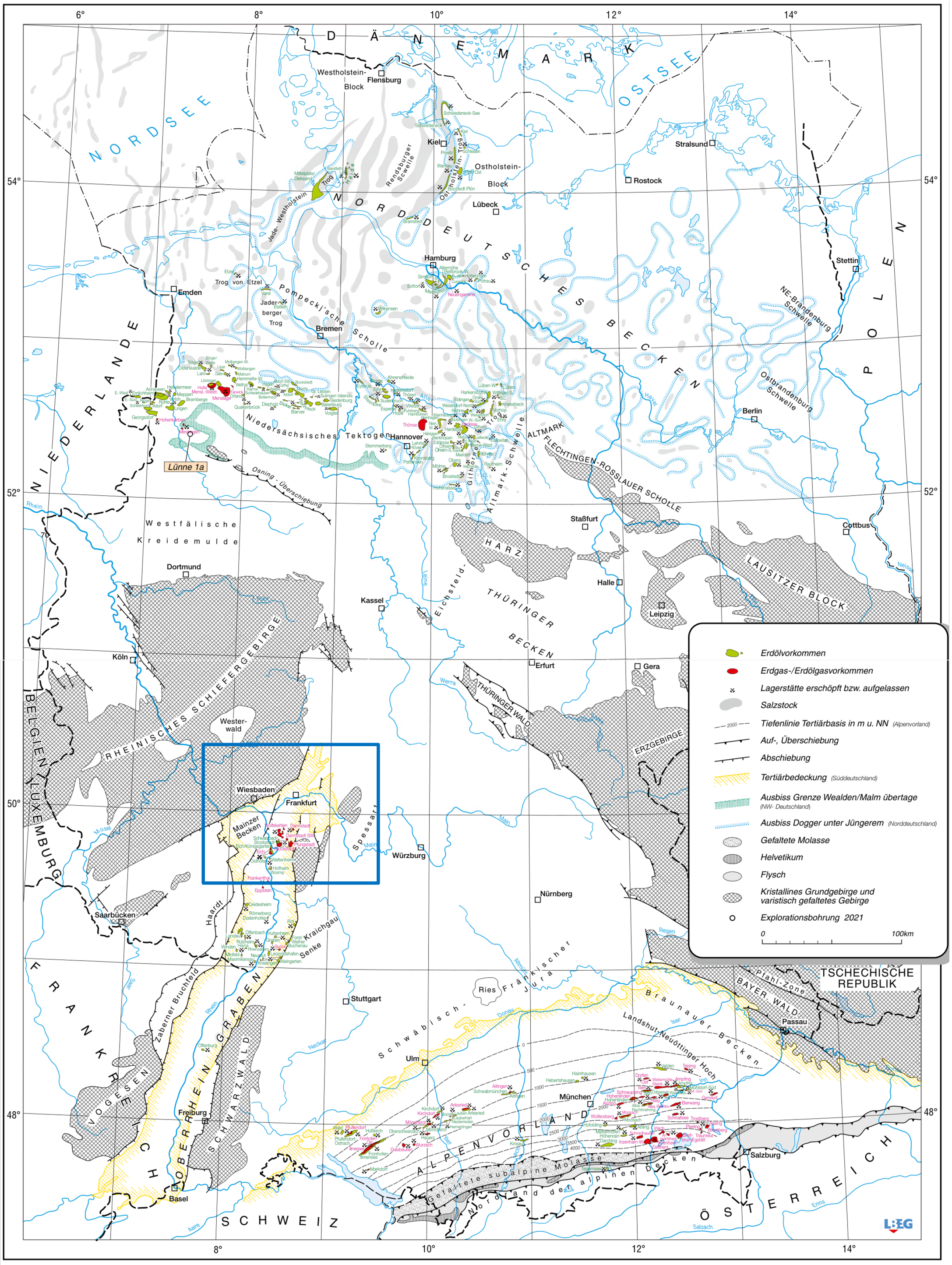


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Figure 21: Oil and gas fields in Germany and exploration wells of the year 2021, floor: Rhaetian, Jurassic, Cretaceous and Cenozoic[41].

8. Surface facilities

Andrews & Shabani[42] gave a comprehensive insight about the basic plan for the infrastructure required for making hydrogen easily accessible to mass. The paper discusses both the hierarchy of spatially-distributed hydrogen production facilities, storage and distribution centers relying on local renewable energy sources and feedstocks would be created to limit the required hydrogen pipeline network to the main metropolitan areas and regions by complementary use of electricity as a major energy vector.

The authors proposed six principles to guide the role played by hydrogen in sustainable energy strategies, both globally and at national levels:

- A hierarchy of sustainable hydrogen production, storage and distribution centers relying on local Renewable energy (RE) sources producing hydrogen as required
- Complementary use of hydrogen and electricity as energy vectors to minimize the extent of new hydrogen pipeline distribution networks
- Production of hydrogen from a range of RE sources and feedstocks, without dependence on nuclear fission power or CCS, but with the application of energy efficiency measures to the economic limit across all sectors of the economy
- Recognition of the complementary roles of hydrogen and battery storage across a range of transport vehicles and transport services
- Use of hydrogen for longer-duration energy storage on centralized grids relying extensively on RE inputs
- Employment of bulk hydrogen storage as the strategic energy reserve to guarantee national and global energy security in a world relying increasingly on RE.

The authors are commenting on the fact that an exclusive ‘hydrogen economy (HE)’ has passed, since electricity and batteries would be used extensively. They are suggesting a ’Hydrogen In a Sustainable Energy’ (HISE) strategy. HISE is set firmly in the context of a zero greenhouse gas emission economy in terms of both the production of hydrogen from renewables and consumption, rather than just as a response to depleting reserves of fossil fuel. While HE involved centralized production of hydrogen from mainly solar and wind energy occupying vast areas of generally remote land, as well as nuclear fission reactors, and hence very long distance transmission of hydrogen via pipelines to centers of consumption, HISE involves decentralized distributed production of hydrogen from a wide variety of renewables and feedstocks.

Figure 22 shows an outlay summarised in the paper of decentralised system for hydrogen production, storage and distribution centers. Off-shore Hydrogen Center (OHC) is designed to produce hydrogen from electrolysis of sea water relying on wave. tidal stream, and/or wind. There is possibility of designing integrated off-shore structures that support both wave energy conversion systems and off-shore aerogenerators with both feeding power directly to the main grid and the surplus to electrolyzers for hydrogen production. The sea water electrolyzers would be required as an integral part of OHCs. Large-scale facilities for the bulk storage of the hydrogen produced by a Coastal Hydrogen Center (CHC), and via subsea pipeline by an OHC too, would be located near to the CHC, e.g. depleted natural gas or oil reservoirs, aquifers, excavated rock caverns and solution-mined salt caverns. The required installations for these kinds of storage are discussed in Section 10.5. Electrolysis of sea water is an option for CHC, otherwise fresh water electrolysis is the next viable option.

In addition or alternatively, the main options for land surface-based large-scale hydrogen storage facilities are compressed gas facilities at pressures up to 700 bar, bulk solid state storage facilities based on metal or chemical hydrides, or carbon-based materials. It would be desirable further to have CHCs and associated hydrogen storage facilities close to major cities to minimize the length of pipeline required for transmission of hydrogen to fuelling stations for transport applications e road, rail, sea and air. Hydrogen directly from the electrolyzers and as needed from storage would also be fed to fuel cell power stations for inputting into the main grid when primary RE power generation was not sufficient to meet demand.

Solar radiation used for production of electricity in photovoltaic or solar thermal systems producing electricity, heat, wind power, biomass and geothermal energy would the resources for Inland Hydrogen Center (IHC). Autonomous hydrogen centers (AHC) would be distributed throughout the more remote and low population density areas of a country, or integrated into new residential and commercial development sites, agricultural and industrial facilities located some distance from the centralized electricity grid. Electricity for direct use would be produced from solar and wind power, with excess over demand being used to produce hydrogen by electrolysis of fresh water. Hydrogen would also be produced from local non-food biomass resources as at IHCs, and possibly in time by photolysis of fresh water directly from solar radiation.

In case of gas mixtures, where two or three gases are produced together, H_2 can be extracted or purified by installing Pressure Swing Adsorption (PSA) technology. This technology is also used in the hydrogen production facilities for purification.

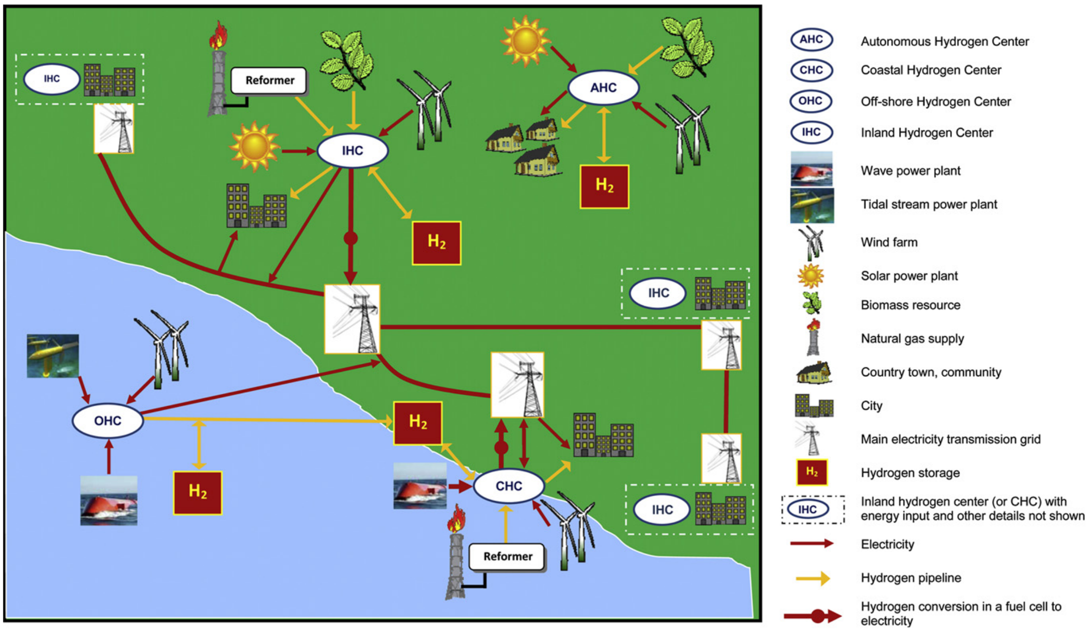


Figure 22: A schematic illustration of the proposed hierarchy of sustainable hydrogen centers showing the principal RE inputs to each type of centre, the local hydrogen distribution system, and the interconnection of higher-order centers via the main electricity grid.[42]

9. Challenges

The most significant challenge with the hydrogen technology is the acceptance of the mass for this field, and the reason to is lack of enough data to validate, and real life examples. Also the cost of the technology is very extravagant in comparison to fossil fuels. This section describes the different aspects of underground storage which require further research attention and lack of it can end into severe challenges in future operations.

9.1. Hydrodynamical properties

The review paper by Muhammed et al.[43], reported the influencing parameters in context of UHS studied by several researchers. The paper categorises the parameters in three broad factors: i) solid factors, ii) fluid factors, and iii) solid-fluid factors. Figure 23 shows further sub parameters categorised in the mentioned factors.

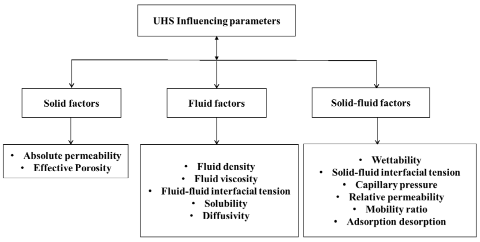


Figure 23: UHS and its influencing parameters[43].

Solid factors: Many authors reported the relationship between effective stress (σ_{eff}) with absolute permeability (k_a) and effective porosity (ϕ_{eff}) due to injection and withdrawal cycle in reservoirs. It has been reported that $k_a/\ \phi_{eff}$ decreases with σ_{eff} during loading cycles for all the rock sample whereas $k_a/\ \phi_{eff}$ increases again with σ_{eff} during unloading. The magnitude of change is smaller for ϕ_{eff} than k_a. However, since H_2 is considered as a very light gas with a higher diffusion propensity on the rock wall, therefore, diffusion can occur even in different pore conditions, and as such quantifying such effect is essential through studying the dispersion–diffusion of H_2 in saturated reservoir conditions and rock type.

Fluid factors: The change in density of H_2 is not significant with increasing pressure and temperature, as it is in case of CH_4 and CO_2, refer Table 9 and Figure 32 (Appendix A). It can be concluded that for a given storage site or pore volume only about 10% by mass can be stored in hydrogen storage operation when compared to natural gas storage operation, requiring significantly bigger dimensions to store equal energy content[29]. Also in subsurface conditions, the density of H_2 is very low in comparison to water, which can lead to strong gravity segregation effect. This implies that during UHS operations, there will be greater upward movement of H_2 towards the caprock.

Table 9: Density changes for H_2 , CO_2, CH_4 due to the changing pressure and temperature.

	Density Change (kg/m^3)	Thermophysical conditions
H_2	0.4–12	0.5 MPa–16 MPa, at 298 K
CH_4	0.6–136	0.2 MPa–20 MPa, at 323 K
CO_2	1.5–784	0.2 MPa–20 MPa, at 323 K

Table 10 summarises the change in viscosity due to increasing pressure for H_2, CH_4, and CO_2. At lower pressure, all three gases have comparable magnitude of viscosity whereas it increases significantly for CH_4 and CO_2 with increasing pressure. This is due to the density of the other two gases because denser fluids have more robust collision and friction between molecules. And temperature increase can lead to low viscosity due to reducing friction between gas molecules. Similarly, water has one to two orders of higher magnitude of viscosity than hydrogen at same pressure-temperature conditions.

Table 10: Viscosity changes for H_2 , CO_2, CH_4 due to the changing pressure and temperature.

	Viscosity change (10^{-3} mPa s)	Thermophysical conditions
H_2	10.4–11.8	0.1 MPa–50 MPa, at 373 K
CH_4	13.6–26	0.1 MPa–48 MPa, at 373 K
CO_2	15.1–138.6	0.1 MPa–50 MPa, at 298 K

This explains the occurrence of viscous fingering (Figure 24) during the injection of hydrogen. In subsurface, when hydrogen is injected in the a brine filled heterogeneous reservoir. Gradually, the low viscous fluid (hydrogen) will penetrate with finger-like patterns into the high viscous fluid (water). The flow can become unstable. This instability arises due to the difference in fluid viscosities and the heterogeneous nature of the porous medium. Heterogeneous porous media refer to materials with variations in permeability or pore structure, leading to variations in fluid flow paths. The displacing fluid flows faster through the high permeable streaks in comparison to the low permeable ones. Viscous fingering is influenced by several factors, including the viscosity contrast between the fluids, the flow rate, the geometry of the porous medium, and the interfacial tension between the fluids.

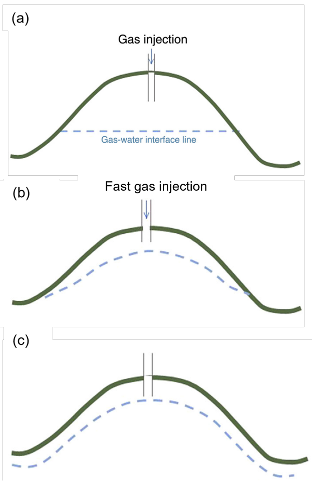


Figure 24: Viscous fingering effect with the injection of hydrogen into an underground deposit: (a) Slow injection, gravitational forces dominate; (b) Fast injection, viscous forces dominate, fingering; (c) Gas spilling due to fingering[44].

Consequently, any small perturbation of the initial plane interface between gas and liquid leads to gas penetration into water in the form of fingers, with the consecutive fast development of fingers[7]. The displacement of methane by hydrogen (gas–gas, no viscous instability) is up to 10 times faster than the displacement of water by hydrogen (due to the viscous fingering)[44].

Basniev et al.[45] suggested to store a mixture of hydrogen and carbon dioxide because the dynamic viscosity coefficient of such mixture is higher than the dynamic viscosity coefficient of pure hydrogen and is close to methane, refer Figure 25 and 32.

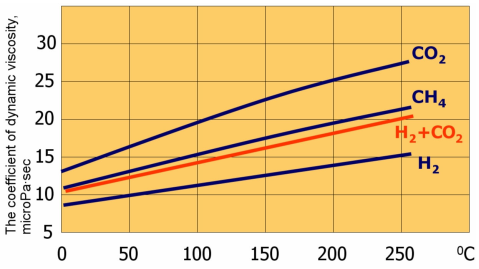


Figure 25: The dependence of viscosity from temperature at atmospheric pressure[45].

Interfacial tension (IFT or γ_{FF}) determines the mixing potential between two fluids. This can impact on the recovery of injected hydrogen, leading to trapped H_2 in isolated pockets. The interfacial tension between the phases is a critical feature of the phase boundary, as it measures the amount of energy necessary to produce more boundary surface. Table 11 and Figure 33 summarises the change in interfacial tension due to pressure and temperature changes. $\gamma_{H_2-H_2O}$ decreases insignificantly (72 mN/m to 68 mN/m) with increasing pressure (0.5 MPa to 45 MPa, constant temperature 298 K) whereas decreases drastically (72 mN/m to 44 mN/m with rising temperature (298 K to 448 K, constant pressure 20 MPa). $\gamma_{CH_4-H_2O}$ exhibits similar behaviour to $\gamma_{H_2-H_2O}$, however it decreases significantly (67 mN/m to 57 mN/m) with increasing pressure (0.1 MPa to 20 MPa, constant temperature 323 K) and does not decrease much (64 mN/m to 62 mN/m with increasing temperature (300 K to 353 K, constant pressure 10 MPa). However, $\gamma_{CO_2-H_2O}$ shows opposite behaviour with increasing temperature (300 K to 353 K, constant pressure 10 MPa), it increases from 25 mN/m to 35 mN/m. But decreases drastically (68 mN/m to 24 mN/m) with increasing pressure (0.1 MPa to 20 MPa, constant temperature 323 K).

Table 11: IFT changes for H_2 , CO_2, CH_4 due to the changing pressure and temperature.

	IFT (mN/m)	IFT (mN/m)
H_2-H_2O	72–68 (0.5 MPa–45 MPa, 298 K)	72–44 (298 K–448 K, 20 MPa)
CH_4-H_2O	67–57 (0.1 MPa–20MPa, 323 K)	64–62 (300 K–353 K, 10 MPa
CO_2-H_2O	68–24 (0.1 MPa–20 MPa, 323 K)	25–35 (300 K–353K, 10 MPa)

The solubility of hydrogen in different co-existing fluids has been reviewed and summarised in the review paper of Muhammed et al.[43]. The review paper reports about experiments showing the solubility behaviour in aqueous and non aqueous solution (diesel) in UHS conditions. Hydrogen solubility in water increases with increasing pressure, and decreases with increasing temperature and increasing salinity. Most researchers emphasized on studying the solubility of hydrogen in subsurface conditions, as this could lead into loss of hydrogen.

Under standard conditions, hydrogen (5.13×10^{-9} m^2/s at 25°C) has almost a three times higher diffusion coefficient in water compared to methane (1.85×10^{-9} m^2/s at 25°C)[8]. The review report by Muhammed et al.[43] mentions about the experimental observations of decrease in H_2

diffusivity with increasing carbon atoms and also concludes that H_2 loss by diffusion is more important in aquifers than in hydrocarbon depleted reservoirs. However, if the cap rock is water-saturated or brine-saturated, the likelihood of dissolution is low due to the limited solubility of hydrogen, which decreases with increasing salinity[7].

Solid-fluid factors: Wettability is defined as a fluid's tendency to adhere to a solid (rock) surface in the presence of other immiscible (or partially miscible) fluids and is determined at the pore scale by the local contact angle (the angle formed by the interface between two fluid phases with the solid, usually measured through the denser phase) (refer Muhammed et al.[43] for original reference). Wettability (contact angle) changes can lead to change in the pore system (adsorption). It is an important entity for estimating storage capacity (C), H_2 saturation, injection and withdrawal rates and containment security. It can be also used for pore-scale modeling (micro-scale) to estimate upscale capillary pressure (Pc) and relative permeability (K_r)[43].

Though, there is very few published data related to the measurements for systems containing rock/brine/H_2, Muhammed et al.[43] compiled the published experimental data and reported in the review article. The review article should be referred for a thorough read. Some of the important graphs and comments is presented in this report. Figure 34 in Appendix A shows the change in contact angle (rock/brine/H_2 wettability) on clay minerals (kaolinite, illite, and montmorillonite) and basaltic rock calculated via the Young's equation, increasing with pressure at a constant temperature.

The rock-gas interfacial tension is a function of pressure, temperature, and acid content, as shown in Figure 33. According to the experimental results, the rock-H_2 IFT ($\gamma_{rock-\mathrm{H_2}}$), rock-$CO_2$ IFT ($\gamma_{rock-\mathrm{CO_2}}$), and rock-$CH_4$ IFT ($\gamma_{rock-\mathrm{CH_4}}$), dropped with pressure and temperature for cleaned quartz Figure 33(a), and the $\gamma_{rock-\mathrm{H_2}}$ and $\gamma_{rock-\mathrm{CO_2}}$ reduced similarly for basaltic rock Figure 33(b). At constant pressure and temperature, $\gamma_{rock-\mathrm{H_2}}$ and $\gamma_{rock-\mathrm{CO_2}}$ decreases with the increase in stearic acid concentration, as seen in Figure 33(c).

Capillary pressure (Pc) is usually combined with relative permeability curves (both as a function of water saturation) to evaluate fluid movement, pore-scale fluid configurations, and the general flow geometry (Al-Khdheeawi et al., 2018; Luboń and Tarkowski, 2020, for original reference[43]). The pressure required to displace this brine is the Pc, and thus it is more favorable in UHS operation to have a high H_2 saturation ($S_{\mathrm{H_2}}$) or low water saturation (S_w) which will result into a larger storage capacity in the rock pores. To determine the surface tension and contact angle for the H2-water sandstone system for the entire water saturation range, the authors combined (through fitting) both capillary pressure data obtained via modified semi-dynamic technique with mercury injection measurement and thereafter, surface tension and contact angle of 51 mN/m and 21.56° (at 5.5 MPa, 20 °C shallow condition) and 46 mN/m and 34.9° (at 10 MPa, 45 °C, deeper condition) respectively were determined for both potential UHS scenarios[46]. However, while the core flood has been performed at primary drainage condition (i.e., initial H_2 injection), the obtained water receding contact angles ($\theta_r = 21.5°$ for shallow, and $\theta_r = 34.9°$ for deep) when evaluated on the modified Morrow curve to get the representative advancing angles does not fully represent the case of H_2 as the non-wetting phase (since θ_a will be far greater than 100° see Figure 26).

Relative permeability (k_r) can behave as a function of saturation depending on the history of the system. This process, also known as hysteresis, is observed during drainage operation where a non-wetting phase (e.g., H_2) is injected to increase the gas saturation in the reservoir. Afterward, an imbibition process is accompanied by the withdrawal of gas to reduce the gas saturation. Each of these processes (drainage and imbibition) has a different trapping system for H_2 thus account for the difference in the (k_r), curves.

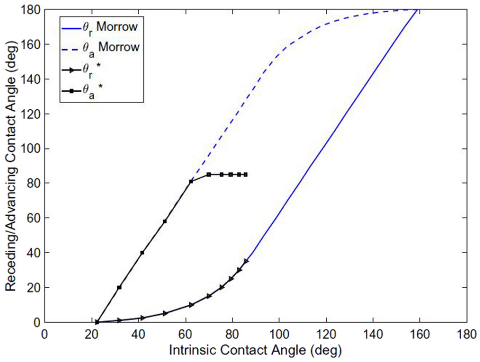


Figure 26: Relationship between receding θ_r and advancing θ_a contact angles as a function of intrinsic θ_i contact angle (Hashemi et al., 2021a). *Denotes the $\theta_r = 12°$ and $\theta_a = 85°$ benchmark data by Hashemi et al.. For original data source refer[43].

The same principle applies to Pc during fluid flow in the porous media as it shows the different behaviors of drainage and imbibition during a storage operation. Pc controls the fluid distribution in the pore space and since it is path-dependent (Raeesi et al., 2014, refer[43]), different cycles or loops (hysteresis) are observed for the drainage (H_2 injection) and imbibition (H_2 withdrawal). Figure 27 shows the dependency of (k_r) on saturation, Muhammed et al.[43] reports the observation from the study carried out by Yekta et al.[46].

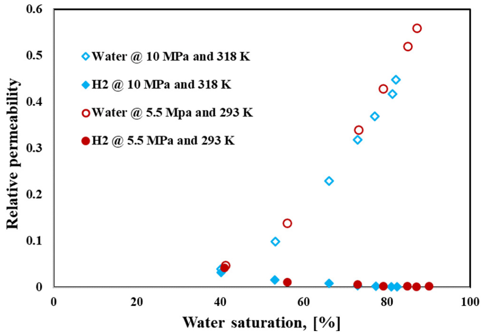


Figure 27: Relative permeability for the H2 water system. At 293 K and 5.5 MPa, relative permeability for H2 (kr-H2) increased from 0 to 0.04 when Sw decreased from 90% to 40%: whereas at 318 K and 10 MPa UHS conditions, kr-H2 again increased from 0 to 0.03 when Sw decreased from 81% to 40%.Source: Data obtained from Yekta et al.[46]

Mobility ratio (M) can be expressed in terms of relative permeabilities and fluid viscosities of displacing (k_{r1}, μ_1) and displaced fluid (k_{r2}, μ_2), which can be expressed by the following equation

$$M = \frac{k_{r1}\mu_2}{k_{r2}\mu_1}$$

In displacement process, it is accepted that mobility ratios < 1 result in a stable displacement, whereas mobility ratios > 1 become unstable, and viscous fingering occurs in the displacement front (Hagemann, 2018, refer[43]). This will result in low H_2 sweep efficiency and inefficient displacement of formation brine (Berg and Ott, 2012, refer[43]).

Gas adsorption-desorption mechanisms take place in micropores with the mesopores or macropores providing storage for the free gas and tortuous paths for gas transport (Afagwu et al., 2021a,b; refer[43]). Same as other hydrodynamical parameters, it is also scarcely studied (Iglauer et al., 2021a; Bardelli et al., 2014; López-Chávez et al., 2020; Didier et al., 2012; refer[43]). The researchers confirmed that A_{H_2} is a function of surface area, pressure, and temperature. Figure 28 illustrates that at greater pressures and larger surface areas, A_{H_2} is higher. Similarly, at constant pressure with increasing temperature, there is a slight increase in adsorption.

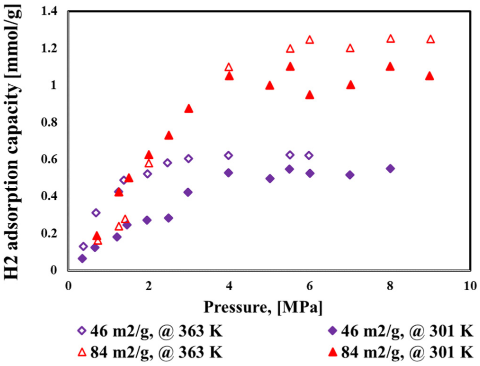


Figure 28: H2 adsorption capacity for clay rocks (Bardelli et al., 2014, refer[43]).

9.2. Subsurface reactions

Abiotic reactions: The chemical reactivity of hydrogen gas (H_2), which is restricted to redox reactions, is kinetically limited due to the polar nature of the molecule and the strong binding energy of the H–H bond (436 kJ/mol) which requires overcoming a very high energy barrier before a possible electronic transfer can take place. Therefore, most possible hydrogen-induced redox reactions are considered negligible at low temperature, even on a geological time scale, as long as no catalyst (or bacteria) is present[33]. Nonetheless, despite the mentioned kinetic limitations, there are some redox reactions induced by H_2 that are feasible at low temperatures such as pyrite reduction (FeS_2) in pyrrhotite (FeS_{1+x}). The minimum temperature for the reaction is 90°C as experimentally demonstrated (Chowdhury, Pal, Papinue, & Lentz, 2020, refer[33] for original citation).

$$FeS_2 + (1-x)H_2 \longrightarrow FeS_{1+x} + (1-x)H_2S$$

where, $(0 < x < 0.125)$

The speed of reaction remains significant even at 50°C, pressures above 30 bar and a pH in water above 8 (Truche et al., 2013, refer[33] for original citation). This reaction leads to the production of H_2S, which can modify the reduction potential and the pH of the water in the porous medium, and this can affect, among others, the microbial population[33].

Heinemann et al.[47] explain the possible hydrogen-brine-rock geochemical reactions, which can take place due to hydrogen injection into a porous reservoir, leading to change in chemical equilibrium between the formation pore water, dissolved gases and the rock matrix. And this could result into: (i) significant loss of hydrogen; (ii) contamination of the stored hydrogen by the production of other gases (e.g. H2S); (iii) mineral dissolution/precipitation leading to enhanced or reduced injectivity; (iv) mineral dissolution leading to opening of migration pathways through the caprock; and (v) mineral dissolution impacting the mechanical properties of the reservoir and the caprock. Dissolved hydrogen does not directly affect the pore water pH. However, it may react with chemical components initially present in the pore water, such as dissolved sulphate, indirectly impacting fluid pH, thereby driving mineral dissolution/precipitation reactions.

Many researchers including Heinemann et al.[47] report hydrogen-driven redox reactions with iron-bearing minerals such as hematite, goethite or with $Fe_3{}^+$-bearing clays and micas can occur, which can change the mechanical strength of the rock matrix and can create new leakage pathways. Also dissolution of sulphur species or sulphur-bearing minerals can impact porosity, permeability, mechanical properties and the generation of H_2S can compromise the purity of stored hydrogen. H_2S can modify the redox potential and the pH and lead to fluid-rock reactions and infrastructure corrosion.

Heinemann et al. also summarise experimental studies (refer[47] for original citation) reservoir sandstones under subsurface conditions ($T = 40–100$ °C, $P = 10–20$ MPa) showing dissolution of carbonate and sulphate cements, results in porosity increase. Similar experiments on reservoir and caprock material of a natural gas storage site show overall decrease in permeability in both rock types, due to the alteration of clay minerals.

Al-Yaseri et al.[48] conducted X-ray computed micro-tomography (mCT) scans of limestone and dolomite cores before and after pressurization with hydrogen for 75 days at 700 psi and 75 °C. They reported significant calcite expansion resulting storage capacity reduction (i.e., effective porosity) by 47%. However, the storage capacity of the dolomite rock slightly increased ($\sim$6%) because the grain expansion effects canceled out the dissolution effects.

Bo et al.[49] performed geochemical modeling using PHREEQC (Version 3) to investigate the potential hydrogen loss associated with hydrogen dissolution and fluid-rock interactions. Also performed geochemical modeling in two commercial gas storage reservoirs (Tubridgi and Mondarra) in Western Australia. The reservoirs are sandstones. The first modeling results exhibits that saturated hydrogen aqueous solution almost does not react with silicate and clay minerals, which is favorable for UHS in quartz-rich sandstone reservoirs. However, unlike silicate and clay minerals, carbonates like calcite triggers up to 9.5% hydrogen loss due to calcite dissolution induced hydrogen dissociation process. Kinetic simulations show that Tubridgi only leads to 0.72% of hydrogen loss, and Mondarra causes 2.76% of hydrogen loss as a result of reservoir calcite dissolution and hydrogen dissociation in brines in 30-year time.

Evaluating the reactivity of hydrogen with carbonate minerals is emphasized by many researchers as a means to mitigate risks associated with hydrogen storage projects in carbonate formations.

Biotic reactions: There are four hydrogenotrophic biotic reactions which are widely discussed or reported by several researchers. Figure 29 illustrates the four main kinds of bacteria consuming hydrogen in UHS and Table 12 summarises its impacts and other characteristics related to the bacterial activity.

- Methanogenesis is a reaction carried out by methanogenic Archaea from hydrogen and CO_2 generating methane. *Methanobacteriales, Methanococcales, and Methanomicrobiales* are the groups belonging to methanogenic Archaea which thrive in anaerobic conditions. CO_2 in the reaction can be have three origins: i) as a component for town gas (10–20% CO_2 and CO), ii) CO_2 from carbonaceous rocks and iii) acetate produced by hydrogenotrophic bacteria, later decomposed by other bacteria into methane and CO_2.

- Acetogens use hydrogen and CO_2 to generate acetate and water. Acetogenic bacteria include: *Clostridium thermoautotrophicum, C. aceticum, Butyribacterium methylotrophicum, Sporomusa sphaeroides, S. ovata, Acetogenium kivui, Acetobacterium woodii*, and other species.

$$4\,H_2 + 2\,CO_2 \longrightarrow CH_3COOH + 2\,H_2O$$

- Sulfate reducers are *Archaeoglobus*, anaerobic and reacts with hydrogen and sulfate anion to produce H_2S gas and water.

$$5\,H_2 + SO_4{}^{2-} \longrightarrow H_2S + 4\,H_2O$$

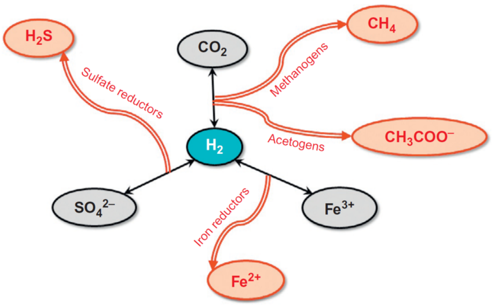


Figure 29: Four types of hydrogenotrophic bacteria acting in UHS, reactions and products[7].

- Iron reducers are anaerobic bacteria reacting directly with the reservoir rocks to reduce ferric ion to ferrous state, it also uses CO_2 and organic substances to fix carbon. *Geobacter metallireducens* and *Shewanella putrefaciens* belong to iron reducing bacteria.

$$H_2 + Fe_2O_3 \longrightarrow 2\,FeO + H_2O$$

A UHS possesses an additional mechanism which causes natural separation of chemical components (hydrogen and methane) in space, which may play both a positive role (an opportunity to extract pure components from different wells) and a negative role (reduction of the total degree of hydrogen enrichment by methane)[50].

Table 12: Main storage impact, hydrogen consumption, and growth conditions for cultivated hydrogenotrophic methanogens, hydrogenotrophic sulfate reducers, homoacetogens and hydrogenotrophic iron(III)-reducing bacteria. Optimum conditions is where the growth peaks; critical is the maximum conditions beyond which no growth is possible[47].

Class of microorganism	Main storage impact	Hydrogen consumption (nM/hour)	Temperature (°C)	Salinity (g/L)	pH
Methanogens	H_2 loss by CH_4 production, clogging	Laboratorial: $0.008–5.8\times10^5$ Oil and gas fields: 0–1185 Wells: up to 4533	Optimum: 30–40 Critical: 122	Optimum: <60 Critical: 200	Optimum: 6.0–7.5 Critical: 4.5–9
Sulfate reducers	H_2 loss by H_2S production, corrosion, clogging	Laboratorial: $0.005–130\times10^5$ Oil and gas fields: 0.05–351 Wells: up to 2544	Optimum: 20–30 Critical: 113	Optimum: <100 Critical: 240	Optimum: 6.0–7.5 Critical: 0.8–11.5
Homoacetogens	H_2 loss by CH_3COOH production, clogging	Laboratorial: $0.2–5.0\times10^5$	Optimum: 20–30 Critical: 72	Optimum: <40 Critical: 300	Optimum: 6.0–7.5 Critical: 3.6–10.7
Iron(III) reducing bacteria	H_2 loss by Fe(II) Production, clogging	Laboratorial: $0.005–2.2\times10^5$	Optimum: 0–30 Critical: 90	Optimum: <40 Critical: 200	Optimum: 6–7.5 Critical: 1.6–>49

9.3. Infrastructure

Melaina et al., 2013[33] discusses about the possible damage to the integrity and durability of metal pipelines caused by exposure to high pressures and hydrogen concentrations over long periods. The impacts of hydrogen on steel alloys (embrittlement) are the possible formation of blisters on the surface, leading to internal cracking and brittleness of the metal. These damages are caused by the high hydrogen diffusivity, whose small atoms are adsorbed to the surface, accumulating and forming molecules, increasing the mechanical stress on the wall that leads to the formation of cracks. This can be practically suppressed by using austenitic steels with 18% chromium and 8% nickel (Duplex stainless steel, 300 series) or chromiummolybdenum blended stainless steels (refer Liebscher et al.[29] for original citation). Most of the elastomer materials used in natural gas distribution systems are compatible with hydrogen (Melaina et al., 2013). However, hydrogen blends can cause problems (e.g., they can influence the accuracy of existing gas meters).

Compressors are an essential part in the gas distribution infrastructure. Liebscher et al.[29] mentions about the traditional lubes of the bearings composed of hydrocarbon products, which decomposes rapidly due to the reaction with H_2.

9.4. Cost efficiency

According to the IRENA Report (2022)[18], hydrogen economy is facing the chicken-and-egg problem. It implies that without demand, investments remain too risky for wide-scale production that could reduce costs; but without economies of scale, the technology remains too costly. The production of hydrogen in electrolyzers is the stage that represents the highest capital expenditure with approximately 80 % of the total in a PtG system[33]. Steam reforming is cost efficient method to produce Hydrogen, approximately 2$/kg, but has disadvantage of producing greenhouse gases as by-product. Water hydrolysis remains about 4 times more expensive, even if renewable electricity sources result in a low or even negative price of electricity at some hours of the day[22]. The cost of electricity to run the compressor units used to store quantities of hydrogen represents a major portion of the operating costs incurred[51]. The requirement of cushion gas in porous-medium storage is also an one-time costly expenditure. Hence, some researchers recommend for the cheaper alternative, such as inert N_2 or CO_2[39].

10. Case studies

This section briefly describes the examples of existing underground storage, pilot projects and feasibility studies worldwide. An attempt has been made to brief all kinds of examples related to pure hydrogen storage, town gas, natural gas, modeling studies related to underground storage and site development feasibility study.

10.1. Pure hydrogen[8][7][29]

There are four known example of underground subsurface storage for pure hydrogen, often mentioned in scientific literature: (i) Teesside in Yorkshire, UK, (ii) Clemens, USA, (iii) Moss Bluff, USA and (iv) Spindletop, USA. The technical parameters of the sites is tabulated in Table 13, giving an overview of the depths, pressure range, storage volume and working gas capacity. The common characteristic of all four sites is that the storage are in salt structure. Teeside in Yokshire, UK is operated by Sabic Petroleum since 1972, it stores pure hydrogen (95% H_2 and 3–4% CO_2) in three salt caverns which are utilized by nearby industrial plants during production of ammonia and methanol. The salt caverns are located in Upper Permian bedded salt deposits and ellipsoid in shape.

In comparison to the site in the UK, the other three salt structures in Texas, USA are relatively deep-seated. Clemens salt dome operated by ConocoPhilips, is in operations since 1983. Clemens salt dome consists of three salt caverns, storing 95% hydrogen and it is connected to the Old Ocean refinery. It has a cylindrical shape, which is 300 m high and has a diameter of 49 m. Praxair is operating Moss Bluff salt cavern since 2007, it is connected to the Praxair Gulf Coast hydrogen pipeline network for the petrochemical needs of Texas and Louisiana. The salt cavern is 580 m high and about 60 m in diameter. The newest Spindletop cavern (operated by Air Liquide since around 2017) is currently the largest hydrogen storage facility in the world.

Table 13: Information about existing hydrogen storage salt caverns in the United Kingdom and the United States. Compiled by Małachowska et al.[8].

	Teesside (UK)	Clemens (US)	Moss Bluff (US)	Spindletop (US)
Salt formation	Bedded salt	Salt dome	Salt dome	Salt dome
Operator	Sabic Petroleum	ConocoPhilips	Praxair	Air Liquide
Commissioned (year)	1972	1983	2007	2017
Volume (m^3)	210,000 (3 * 70000)	580,000	566,000	906,000
Average cavern depth (m)	365	1000	1200	1340
Pressure range (bar)	45	70–137	55–152	68-202
Net energy stored (GWh)	27	81	123	274
Possible working gas capacity H_2 (10^3 t)	0.83	2.56	3.72	Information not available

10.2. Town gas[8][7][29][33]

Town gas or coal gas is generally produced by coal gasification. It contains approximately 50–60 % H_2 and other gases such as CO, CO_2, CH_4 and N_2. Town gas is a more general term referring to manufactured gaseous fuels produced for sale to consumers and municipalities. It was used in Europe during the second half of the 19th century before it was replaced by natural gas. In between 1956 and 1972, Gaz de France (GDF) stored town gas (50% H_2)in a saline aquifer (gray sandstone, capacity 385 Mm^3) at Beynes (Yvelines), France. The authorities did not report any loss of hydrogen during its 18 years of operation. However, intensive bacterial activity is observed in recent times.

The underground reservoir near Lobodice, Czechoslovakia was artificially created in a saline aquifer. It is an anticlinal structure of Miocene age, and the main reservoir is composed of heterogeneous sands, gravels and sandstone at a depth of about 400–500m. In 1990, town gas (H_2 (60 %), CO_2 (10 %), CO (10 %), y CH_4 (20 %)) was stored, which suffered changes during its 7-month storage cycle. The extracted gas, composed of 37 % of H_2, 12 % of CO + CO_2, and 40 % of CH_4, was analyzed; which implied a rise of 20 % of methane and a reduction of H_2, CO, and CO_2. This change in chemical composition was accompanied by a slight pressure decrease in the reservoir that was below the value calculated and predicted by material balance. Part of the extracted methane had an isotopic origin different from injected methane, proving the existence of methane generators. The analysis of the fluid present in the geological formation found populations of methanogenic microorganisms, with a density in the order of 10^3–10^4 cel/mL. A shallow sandstone aquifer (200–250 m) in Ketzin (Germany) had been used for the storage of town gas (62% H_2). Gas losses were reported in the order of 2×10^8 m^3 between 1964 and 1985 over the operative gas volume of 1.30×10^8 m^3. In addition, a change in the composition of the gas, corrosion in the underground facilities, and changes in the permeability of the deposit were observed. The overall picture for H_2 and CH_4 is not that clear but suggests an overall gain of H_2 and CH_4, cannot be explained by simple microbial degradation of the stored hydrogen.

10.3. Natural hydrogen[24]

Prinzhofer et al.[23] reported about the natural occurrence of hydrogen Bourakebougou field, Mali. The stacked reservoir composed of at least five intervals is a shallow reservoir at a depth of 110 m. A Canandian company Petroma (now renamed as Hydroma), in 2012 accidentally found the hydrogen instead of water. The occurrence of hydrogen in the formation is related to the existence of multiple layers of dolerite beds and aquifers.

From 2017 to 2018, the company drilled a total of 24 wells in its mining blocks, in addition to conducting extensive geological, geophysical and geochemical studies. The results show that relatively pure hydrogen reservoirs are associated with trace amounts of methane, nitrogen, and helium. The actual development and utilization of natural hydrogen are only in the Bougou 1 well (hydrogen content is 98%) in the Bourakebougou area of Mali.

The hydrogen production rate of this well was 1.5×10^3 m^3/d in 2012 (Briere D et al., refer[24] for original citation), and the well is still in operation so far. Interesting, fairy circles are absent in this area. Moretti et al.[21] gives an possible explanation related to intracratonic basins whose subsurface is iron rich. It is observed that the hydrogen system has effective seal, a dolerite which explains the absence of fairy circles[23].

The area is covered with deep layers of laterites and locally with ferruginous crust. The ferruginous crust is generally enriched with goethite and hematite due to tropical weathering of laterites. Some researchers (Alpermann et al. refer[21] for original citation) explains from laboratory experiments conducted at high pressure (100 bars) and low temperatures (70 to 120 °C), that hematite has the ability to oxidise H_2 without any biological help and in subsurface conditions.

10.4. UHS modeling studies

Representing geological reservoir in 3D space using open source or commercial softwares is nowadays an essential tool in reservoir characterisation in mining or petroleum industries. Some of these softwares enable the user to capture the heterogeneity of reservoir properties (lithology, porosity, permeability etc.) from acquired data or prior knowledge of analogues using geostatistical algorithms. The 3D models are used for fluid flow simulation, to understand the behaviour of the reservoir under fluid production phase. This workflow is a powerful tool for generating infinite number of hypothetical scenarios for understanding the changing behaviour in terms of pressure and fluid saturation. This workflow is followed in petroleum industry to design the development plan of a field, safe operation of the field and predicting the production.

The same approach is adopted by many research groups across the world for ongoing research and pilot projects related to subsurface hydrogen storage. This enabled the researchers to use the hydrodynamical and geochemical properties of hydrogen and predict the behaviour of hydrogen with rock and formation fluid. Table 17 in Appendix B summarises current research work addressing the UHS modeling topic. Some of the research work is briefly discussed to give an insight to the readers about the potential and importance of these studies.

In the scope of ANGUS+ research project, Pfeiffer and Bauer[52] developed a hypothetical model based on a anticlinal structure in Schleswig-Holstein at a depth between 460–490 m. The structure was formed by halokinesis of the Zechstein salt group which started in the Triassic, and the target reservoir formation was the main sandstone of the Middle Rhaetian. Homogeneous reservoir properties were assumed in the hypothetical model. Nitrogen was injected as cushion gas, as it is chemically inert and cheap due to its abundance in the atmosphere. The simulation was carried out using the multiphase-multicomponent reservoir simulator Eclipse E300 from Schlumberger. Approximately, a duration of 3.5 years was simulated which was divided into three phases: injection of N_2 as cushion gas for 710 days, injection of H_2 as working gas for 210 days, four cycles of extraction(7 days)–injection (50 days)–subsequent shut–in period (30) days. Five wells were used for the simulation. The achievable gas flow rates were constrained by upper and lower bottom hole pressure limits set to 65 and 30 bar respectively. The goal was to yield 27% of the energy demand for the state of Schleswig-Holstein for one week duration. The authors reported in the published paper[52], that it was possible to achieve the extraction rate and yield to supply about 20% of the average demand in electrical energy of the state of Schleswig-Holstein, Germany, for a week-long period.

Further in the same project, Pfeiffer et al.[39], upgraded the hypothetical model by introducing the heterogeneity in the reservoir properties (lithology, porosity and permeability) in 3D space, it was intended to investigate the effect of reservoir heterogeneity on the storage operation. The realizations generated are to obtain a first estimate of the effects of geological formation sub-structure and heterogeneity on the storage operation, especially the pressure evolution and the gas-phase distribution, as well as the well deliverability rates. The authors concluded that the performance of the storage site is mainly governed by the distribution of the H_2 gas phase within the storage formation, which, in turn, depends strongly on the formation heterogeneity.

Bauer et al.[53] further investigated the induced effects of the above mentioned storage due to operation activities. It is found that induced pressure effects may range over kilometers for gas storage, while temperature effects are limited to a few tens of meters for heat storage.

In the second phase of the ANGUS+ project (ANGUS II), Gasanzade et al.[54] analyzed gas leakage through a fault zone during the operation period. The authors used a hypothetical methane gas storage operation for the same anticline structure and simulated it for pressure changes, later the sensitivity analysis for the fault zone parameterisations was carried out on a 2-D slice of the model area. The leakage scenario simulations show a strong parameter dependence with the fault acting as either a barrier or a conduit for gas flow. Change in leakage rates during the injection phase was observed, the rates decrease with increasing capillary entry pressure and decreasing damage zone permeability. The authors suggested about upgrading models like this, by generating fully coupled hydromechanical models by characterisation of site-specific mechanical properties of fault zone, for the study of fault reactivation.

Feldmann et al.[55] studied the hydrodynamic and gas mixing processes in a hypothetical model of one of the largest on-shore gas fields in Europe, as a part of H2STORE research project. The numerical simulation was executed for 10 years (5 years of injection and next 5 years of seasonal cyclic operation). Numerical case studies of hydrogen injection indicated that gravity override and viscous fingering in aquifer structures complicate an efficient displacement of the native fluid. In contrast, both physical phenomena play a minor role in gas saturated reservoirs.

Lysyy et al.[56] did numerical simulation using Eclipse E100 Schlumberger for the depleted oil and gas field of Norne hydrocarbon field, offshore Norway. The field is operated by Equinor Energy AS. The authors wanted to address the scarcity of research work related to converting depleted hydrocarbon fields into hydrogen storage. The simulation was done for four annual storage cycles and one prolonged withdrawal period. Annual hydrogen delivery, cushion gas nature, cushion gas composition and structural geometries were the important aspects which were studied. The important finding was that the pre-injection of formation cushion gas increased the hydrogen recovery factor, however the purity of hydrogen was compromised.

Delshad et al.[57] did two case studies for conversion into hydrogen storage: a depleted oil reservoir in Colorado, USA and CO_2 storage demonstration project in Cranfield formation (saline aquifer) in Mississippi, USA. They used CMG-CEM for the compositional reservoir simulation. Currently majority of the research groups agree to the fact that the experience with CO_2 and methane cannot be directly applied to the H_2, hence the authors calibrated the gas equation of state against published laboratory H_2 density and viscosity data as a function of pressure and temperature. Also, they tried to analyze the effect of relative permeability of multi-component system (including H_2).

The 3D model with dynamic flow simulation is an essential step before developing a structure, irrespective of the kind of fluid stored. Also it is recommended to do a fully coupled hydromechanical simualtion for understanding the stress variation and surface movements due to operation activities. Hydromechanical models are done for studying well bore integrity, fault reactivations, safe operations criteria (pressure) etc.

10.5. Geological site development

Lord et al.[36] did an economic analysis that addresses the costs entailed in developing and operating a geologic storage facility. The work focuses primarily developing salt caverns close to cities to suffice the demand, the authors gave two important reasons for doing so: (1) salt caverns are known to successfully contain hydrogen, and (2) there is more geotechnical certainty involved with salt storage as compared to the other three storage options. However, the paper also provides an initial cost consideration for all types of geological storages. The Hydrogen Geologic Storage Model (H2GSM) is an analytical framework developed to highlight the major components of a 'gate-to-gate' (i.e., storage infrastructure only), large-scale hydrogen storage facility. The H2GSM model has two overarching core components: the geologic storage module and the economic systems module. The city-specific demands, relying solely on storage within salt caverns, are then developed from these modules. The analysis considered geologic basins across the United States of America, which can be well connected with some big cities (e.g. Houston). The salt cavern and hard rock cavern examples were adapted from the ConocoPhillips salt cavern, which currently stores hydrogen in Texas. For the depleted oil and gas reservoir and the aquifer example, the geologic parameters used were adapted from NatCarb (2008) [34] and based on the Yeso Formation within the Estancia Basin in New Mexico. Table 14 illustrates the salient storage characteristics used in the cost analysis assuming a 10% market penetration of a city population similar in size to Houston, TX. The paper includes all the formulas used for calculating the individual costs, listed in Table 15.

Table 14: Geologic Storage Site Design Characteristics[36]

Geologic Storage Site Design Characteristics	**Salt Cavern**	**Depleted Oil & Gas Reservoir**	**Hard Rock**	**Aquifer**
Formation Pressure (Pa)	1.3789×10^7*	1.3755×10^7	1.3789×10^7	1.3755×10^7
Void Volume (m^3)	580,000	676,941	580,000	676,941
Formation Temp. (K)	310.9**	315.1	310.9	315.1
Well Depth (m)	1158	1403	1158	1403
Working Gas (tonnes H_2)	1,912	1,912	1,912	1,912
Cushion Gas percent of Total Volume (%)	30	50	30	50
Cushion Gas (tonnes H_2)	574	956	574	956
Total H_2 Stored on site (tonnes H_2)	2,486	2,868	2,486	2,868

* Assumed to be operating pressure.

** Assumed to be gas temperature. Note: Values represent an example of demand for a city the size of Houston for illustration.

Table 15: Geologic Storage Site Design Characteristics[36]

Cost Analysis Assumptions				
	Salt Cavern	**Depleted Oil & Gas Reservoir**	**Hard Rock**	**Aquifer**
Cushion Gas Capital Cost ($)	**11,227,540**	**21,492,278**	**11,227,540**	**21,492,278**
Cost of H 2 Gas ($/kg)	6	6	6	6
Geologic Site Preparation Total Cavern Site Development ($)	**23,340,000**	**n/a**	**48,720,000**	**n/a**
Mining costs (\$/m^3)	23	n/a	84	n/a
Leaching Plant Costs (M$)	10	n/a	n/a	n/a
Site Characterization (M$)	n/a	n/a	n/a	10.3
Compressor Capital Costs ($)	**27,539,480**	**18,359,654**	**27,539,480**	**18,359,654**
Injection Rate (kg/hr)	2960	2487	2960	2487
Withdrawal Rate (kg/hr)	4920	2487	4920	2487
Compressor Power (kWh/kg)**	2.2	2.2	2.2	2.2
Compressor kWh/yr	988,819	499,836	988,819	499,836
Operating Days/yr**	350	350	350	350
Compressor Capacity Factor (%)**	96	96	96	96
Cost of Electricity (cents/kWh)	5	5	5	5
Levelized electricity cost per compressor ($/kg)	0.002	0.001	0.002	0.001
Water and Cooling Cost/Compressor ($/100 liters)	0.02	0.02	0.02	0.02
Water requirements per compressor (l/kg H 2)**	50	50	50	50
Water and Cooling Costs ($/kg H 2)	0.012	0.012	0.012	0.012
Compressor O&M ($/kg H 2)	0.014	0.014	0.014	0.014
Number of Compressors	3	2	3	2
Compressor Size (kg/hr)	2000	2000	2000	2000
Compressor Size (kW)	3700	3700	3700	3700
Cost per compressor ($/kW)	2481	2481	2481	2481
Pipelines and Wells Capital Cost, Full Pipeline Costs ($/tonne)	**4.39**	**6.26**	**4.39**	**6.26**
Pipeline Fixed Costs ($/tonne)	4.03	4.03	4.03	4.03
System Flow rate (tonne/hr)	4.78	2.42	4.78	4.78
Pipeline Maximum Flow rate (tonne/hr)	445.9	445.9	445.9	445.9
Transport Distance of H 2 (km)	16	16	16	16
Base Transport Distance (km)	100	100	100	100
Well O&M Multiplier (%)	4	4	n/a	4
Number of Injection / Withdrawal wells	1	1	1	1
Capital cost per well (M$/well)	1.15	0.26	2.16	1.15
Well Variable Cost ($/km)	1,434,409	318,757	3,250,547*	1,434,409
Well depth (ft)	3800	4604	3800	3800
Well Variable Cost (M$)	1.66	0.45	1.61	1.66
Equipment Lifetime (years)	30	30	30	30
Discount Rate (%)	10	10	10	10
Capital Recovery Factor	0.11	0.11	0.11	0.11
Full H 2 Well Costs ($/tonne)	46.27	10.55	556	46.27
Mass Flow Rate/day/well	2500	2500	2500	2500
Injection Rate (kg H 2/hr)	283,836	283,479	283,836	283,836
Full H 2 surface piping ($/tonne)	0	0	0	0
H 2 Pipeline and Well Costs ($/tonne)	50.66	16.80	560.46	53.71
Total Capital Costs	**63,254,547**	**40,106,938**	**89,644,020**	**40,999,458**
Levelized Total Capital Costs ($/kg)	**1.54**	**1.19**	**2.18**	**1.21**
Levelized Cost of H 2 ($/kg)	**1.61**	**1.23**	**2.77**	**1.29**

* Calculated using the formula from Mansure and Blankenship, 2010 [35].

** Adapted from Amos, 1998 [36]; Capacity Factor developed from listed compressor operating 350 days per year / 365 calendar days per year.

*** Adapted from Ogden, 2002 and refined in Williams, 2002.

11. Hydrogen strategies of different countries

This section excerpts from the International Renewable Energy Agency (IRENA) report published in 2022. The report consists of the plans announced by different countries to achieve the clean hydrogen goal. Along with this, the outcome of the review paper by Cheng et al.[58] is presented here. The article attempted to categorise the strategies (How much green they are?) based on the text of national hydrogen strategies and relevant literature. The authors mentioned clearly that it is not a attempt of criticism, rather giving an overview how different countries are trying to meet the target of net-zero or clean hydrogen. Both documents report how every country is using carefully the nomenclature related to hydrogen. This reflects diplomatic steps in terms of phasing out fossil fuels and transition to renewable hydrogen. Clean hydrogen, low-carbon hydrogen, hydrogen derivatives and synthetic fuels are the nomenclatures used along with green hydrogen. The terms were used in the strategies to show the transition phase from fossil fuels to clean hydrogen. They cover hydrogen with less methane emissions and very high carbon capture rates, hydrogen without meeting the emission standards, hydrogen made with grid-powered electrolysis with decarbonised grid, hydrogen converted to ammonia, methanol, synthetic fuels or gaseous and liquid fuels produced from hydrogen and carbon[18] (pp. 19).

Why hydrogen is becoming the limelight of energy sector? According to the IRENA report, there are two major factors: first is to reduce the emission rates and avoiding the rise of global temperature 1.5 °C (Paris 2015 Agreement), and the target for achieving net-zero is by 2050. The second reason is that the technological and cost barrier to renewables and electrolzers are reducing, implying that a large volume of green hydrogen can be generated. This, in turn, demands storage facilities for long duration. Japan being the first in 2017, another 30 major world economies have issued national hydrogen strategies. The projection for global hydrogen by 2050 report by different agencies (compiled as graph in Figure 1.1, in IRENA report 2022), suggest that the scenario will change from now (mostly grey hydrogen, no green hydrogen) to intermediate stage of blue and green hydrogen to blue (with CCS) and green. These projections are also reflected in different national strategies as what would be the path to green hydrogen.

Cheng et al. mentioned that in broad sense there are three kinds based on regulatory stringency: Zero regulatory stringency, Scale-first-and-clean-later and Green-hydrogen-now. The categorisation was done by the authors based on temporal parameter, fossil fuel penalties, hydrogen certifications, and innovation enablement. Table 16 lists the countries based on the mentioned parameters.

India being depended on its coal reserves, Norway as the largest natural gas exporter and the US, their strategies are based upon hydrogen development supported by fossil-fuel resources and nuclear power plants. The reason for listing them as zero regulatory stringency group is lack of certification scheme, carbon pricing and exclusive support for renewable hydrogen. However, there are regulatory measures in the US at the subnational level (California). The report also mentions about the lack of nationwide strategy plan of China, however there are some local hydrogen plans available. The scale-first-and-clean-later group has been subdivided considering the regulatory stringency. The low regulatory stringency group has a "balanced" approach for fossil fuel and renewable hydrogen, the strategies lack namely, certification scheme for export or fossil fuel penalties. The medium regulatory stringency group comprises of industrialized nations with solid infrastructure, have decarbonization plan in their strategies. The nations with medium regulatory stringency support explicitly technology neutrality, which implies incremental transitional pathway. The regulatory stringency group have all the regulatory measures, e.g. New Zealand is not supporting CCS technologies and focusing on establishing standards for export. And Portugal is the only country which is considered in "green-hydrogen-now" group, as it has all three regulatory measures and already phased out coal.

The priority of the clean hydrogen strategies and policies (Figure S.3 in IRENA report 2022, pp. 14) is set high for centralised applications such as chemicals, refineries, international shipping, steel, long-haul aviation and seasonal storage. The lowest priority is given to residential heating followed by other distributed applications like short-haul aviation, regional trucks, urban vehicles and short-term storage. Applications like long-haul trucks, high temperature heating, trains and ferries have medium priorities. However, cost, technological maturity, efficiency, sufficient renewable electricity, policy and regulatory uncertainty, standards and certification, and demand-and-investment risks are some major socioeconomic barriers in scaling of hydrogen.

The overview of the national strategies and the respective governments are optimistic and willing to bring the change, Figure 30(a) summarises different kinds of projects announced by several countries. IRENA report 2022 mentions "As of November 2021, global announcements of hydrogen projects by 2030 add up to USD 160 billion of investment, with half of the investments being planned for green hydrogen production using renewable energy sources and electrolysis (Hydrogen Council, 2021)". These investments take into account developing new trade routes, re-purposing natural gas pipelines and constructing pipelines. Figure 30(b) show the overview of in-place, under development and potential bilateral deals among the countries for new hydrogen trade relations. By early August 2021, governments had allocated at least USD 65 billion in targeted support for clean hydrogen over the next decade, with France, Germany and Japan making the most significant commitments (Figure 30(c)). These amounts are sizeable, but they pale in comparison with energy sector subsidies, which amounted to USD 634 billion in 2017, 70% of which supported fossil fuels (IRENA 2020c). It is also interesting to account that the ability to produce large volumes of low-cost green hydrogen varies geographically. Countries' technical renewable potential is not the only factor determining how likely they are to become major producers of green hydrogen. Many other factors come into play, including existing infrastructure and “soft factors” (e.g. government support, business friendliness, political stability) and the current energy mix and industry (e.g. renewable plans, potential demand for hydrogen). For example 'Cost of Capital, the report mentions clearly that in future the energy cost will be dominated by the capital cost. However, if it is assumed that these differences in cost of capital even out (weighted cost of capital or WACC), then the global scenario of trading will change, illustrated in Figure 30(d).

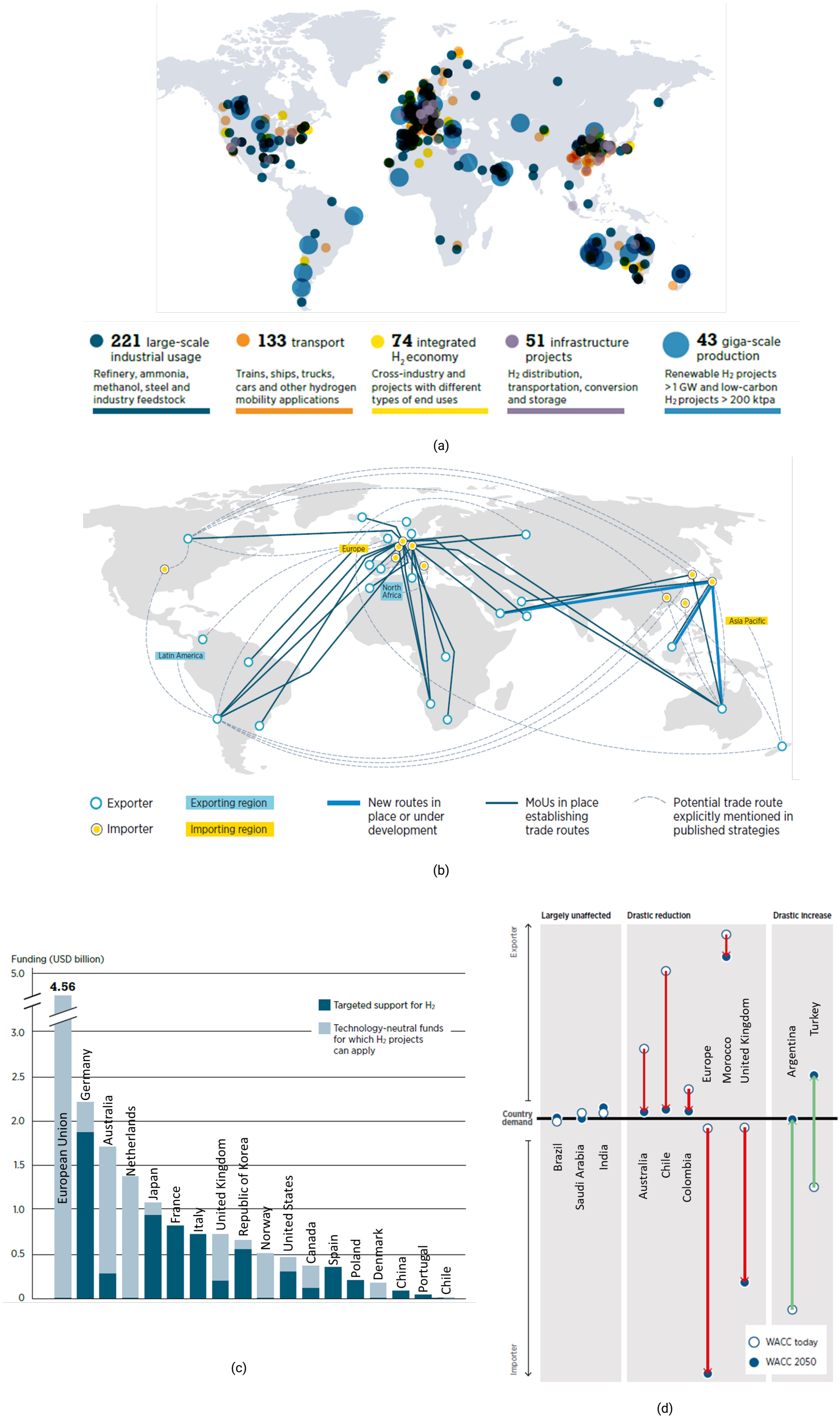
At this juncture, the strategies of importer and exporter countries is crucial. Chile and Morocco being fossil fuel importing countries, have launched their green hydrogen strategy in 2020, and created a National Hydrogen Commission in 2019 respectively. Chile is aiming to become one of the world's top three hydrogen fuel exporters by 2040. To achieve this goal, it has planned milestone of 5GW of electrolyzer capacity by 2025 and 25 GW by 2030, doing so can result in producing cheapest hydrogen by 2030. Morocco plans for a local market of 4 TWh and an export market of 10 TWh, with a facility of 6 GW of new renewable capacity. On the other hand giant fossil fuel exporters such as Australia, Canada, Norway, Oman, Russia, Saudi Arabia and United Arab Emirates are also racing, to reduce the risks of losing energy markets. Australia, Canada and Norway announced strategies emphasizing on "technology-neutral" approach and explicitly included the possibility of blue hydrogen.

Australia has nine gigawatt-scale green hydrogen projects planned or under development, and the government does not rule out the blue hydrogen production. Australia has also forged deals with prospective export markets, such as Germany, Japan, and Singapore. Canada's strategy focuses on the transition to an increasing percentage of renewable or zero-emission production methods and refers specifically to the country's large hydropower capacity. Equinor, a Norwegian energy company, is currently studying the possibility of delivering natural gas to Germany or the Netherlands, where it can be converted into blue hydrogen. Oman is planning to utilise its abundant solar and wind resources in the Al Wusta Governorate and the Arabian sea port of Duqm for exports. According to the there announced projects, the biggest is powered by 25 GW of solar and wind. Russia aims to have 20% of the global hydrogen market, foreseeing export of 50 million tonnes of clean hydrogen (mainly blue). Saudi Arabia announced the Helios Green Fuel Project in July 2020, it is USD 5 billion green hydrogen and green ammonia plant powered entirely by solar and wind. United Arab emirates ambitions to become a leader in blue hydrogen exports by capturing 25% of the global low-carbon hydrogen market by 2030.

Countries like Namibia, having vast solar and wind energy resources are focus for global investors. The government has announced some giant projects related to green hydrogen and the size of these projects is substantially large to Namibia's economy which shows the transformative potential of green hydrogen for the national economy.

Table 16: Identification of regulatory stringency for green hydrogen by groups[58].

Regulatory Stringency Groups		**Countries**
Zero regulatory stringency		India, Norway, the US
Scale-first-and-clean-later	Low regulatory stringency group	Australia, Colombia, Finland, Japan, Paraguay, Poland, Russia, the UAE
	Medium regulatory stringency group	Canada, the Czech Republic, the EU, France, Germany, Hungary, Morocco, the Netherlands, Ukraine, the Republic of Korea, Slovakia, , the UK
	High regulatory stringency group	Chile, Italy, New Zealand, Spain,
Green-hydrogen-now		Portugal



(a)

(b)

(c)

(d)

Figure 30: Complied from the International Renewable Energy Agency (IRENA) report[18] published in 2022: (a) Clean hydrogen projects and investment (November 2021), (b) An expanding network of hydrogen trade routes, plans and agreements, (c) Average annual funding potentially available for hydrogen projects for 2021-2030, as of August 2021 and (d) Impact of cost assumptions on hydrogen production of selected countries.

12. Projects across the world

The world map in Figure 31 illustrates the biggest announced green hydrogen projects on national level, the size of the project refers to the electrolyzer capacity. Governments, companies and universities are also engaging into research and development projects to minimize the uncertainties related to the different aspect of hydrogen economy and making it more affordable. A Commonwealth Scientific and Industrial Research Organisation (CSIRO) publication[59] by Delaval et al. focuses in analysing hydrogen RD&D collaborations and opportunities of ten countries: Canada, China, France, Germany, India, Japan, Republic of Korea, Singapore, United Kingdom and the United States of America. The report highlights research and development activities from every sector such as production, storage and distribution, and utilisation. In this report, research works related to subsurface gas storage are listed and briefly described.

HyUnder project "Assessing the potential, actors and business models of large-scale UHS in Europe" started in the summer 2012 and was carried out for 24 months[60]. The project focused on six European countries (France, Germany, the Netherlands, Romania, Spain and the United Kingdom); it assessed the economic feasibility of converting renewable energy into hydrogen and storing it in large-scale underground storage based on geological and geographical factors.

Hychico began their pilot project in 2010 to test the reservoir's capacity, tightness and behavior to acquire experience in hydrogen storage. It took part into HyUnder consortium from 2012-2014. One of the objectives of the project is to test mixtures of hydrogen and natural gas for supplying equipment between 10 and 30 MW and providing electricity during peak demand times. During the time period of 2016-2018, Hychico started pilot project to produce methane from hydrogen and carbon dioxide by underground controlled methanogenesis. Its purpose was to do a feasibility study for "green methane"[61].

Underground Sun Storage project[62] was initiated by RAG Austria AG in 2013 and lasted until 2017. The aim of the project was to do a full storage cycle of a gas mixture with 10% of hydrogen blend, risk assessment and a life-cycle assessment of such technology with social, legal and economic aspects. The laboratory experiments were conducted based on the geological situation in the Austrian molass basin and took into account the technical conditions of RAG's (RAG Austria AG) commercial gas storage facilities. With this project, RAG Austria could conclude that subsurface storage of hydrogen is possible at a commercial scale with similar geological settings. They successfully tested the gas infrastructure for hydrogen applicability, and no negative influence on the existing storage facility has been reported. Finally, they were able to ascertain that the integrity of porous gas storage is not threatened, as no alteration of the reservoir rock is observed, and microbial processes can be managed effectively.

From the learnings of Underground Sun Storage project, RAG Austria launched the follow up project "Underground Sun Conversion[63]" in March 2017 and submitted the final report in February 2021. The aim of the RAG-initiated project was to carry out research on producing large quantities of renewable gas, using a carbon binding process, and storing it in naturally formed gas reservoirs, which will provide urgently needed flexibility for renewable energy sources. Hydrogen sourced from renewable resources is injected alongside carbon dioxide into an existing natural gas reservoir located in Pilsbach, Upper Austria. Microorganisms consumed both gases through a process known as geomethanation (Sabatier's reaction) to produce methane at reservoir conditions.

H2STORE was a collaborative project started in august 2012, with aim of analyzing sedimentological, petrophysical, mineralogical/ geochemical, hydrochemical, and microbiological features of the different geological strata and German locations to evaluate potential fluid-rock reactions induced by hydrogen injection[64].

In the ANGUS+ project[65] the potentials and implications of energy storage in the geological subsurface were investigated. Within the project, storage formations were characterised by physical and chemical properties, and the processes induced by energy storage applications were parameterised based on literature studies and laboratory experiments. This new parameter database has supported the development and implementation of numerical modeling tools within the project. These tools are used to simulate the coupled thermal, hydraulic, mechanical, chemical, and microbiological processes induced by subsurface energy storage applications and their interaction with other types of geological subsurface uses. ANGUS+ project ran for 54 months(July 2012–June 2017).

The project entered into its next phase called ANGUS II[66] , investigating subsurface storage options for hydrogen, synthetic methane, compressed air and heat or cold - topics already addressed in the preceding project. The main objective of the project was the characterisation of the subterranean geosystem with the yet unstudied hydraulic barriers and related processes. Coupling schemes for existing models for the simulation of energy grids, individual power plants and geotechnical storage sites will be developed and applied to realistic scenarios. The project duration was 48 months (January 2017–December 2020). Schleswig-Holstein was used as a model area for generating the scenarios.

InSpEE-DS project[67] began in October 2015 and finished in September 2019, the focus was to plan bases, selection criteria and potential assessment for the construction of salt caverns for the storage of renewable energies (hydrogen and compressed air) - Zechstein salt structures in northern Germany.

1	**HyDeal Ambition (67GW)**	Western Europe
2	**Unnamed (30GW)**	Kazakhstan
3	**Western Green Energy Hub (28GW)**	Australia
4	**AMAN (16GW)[a]**	Mauritania
5	**Asian Renewable Energy Hub (14GW)**	Australia
6	**Oman Green Energy Hub (14GW)[a]**	Oman
7	**AquaVentus (10GW)**	Germany
8	**NortH2 (10GW)**	Netherlands
9	**H2 Magallanes (8GW)**	Chile
10	**Beijing Jingneng (5GW)**	China
11	**Project Nour (5GW)[a]**	Mauritania
12	**HyEnergy Zero Carbon Hydrogen (4GW)[a]**	Australia
13	**Pacific solar Hydrogen (3.6GW)**	Australia
14	**Green Marlin (3.2GW)**	Ireland
15	**H2-Hub Gladstone (3GW)**	Australia
16	**Moolawatana Renewable Hydrogen Project (3GW)[a]**	Australia
17	**Murchison Renewable Hydrogen Project (3GW)**	Australia
18	**Unnamed (3GW)**	Namibia
19	**Base One (2GW)[a]**	Brazil
20	**Helios green Fuels Project (2GW)**	Saudi Arabia

Figure 31: The world's 20 largest announced giga-scale green hydrogen projects[18].

13. Conclusions

In conclusion, hydrogen technology has the potential to revolutionize the way we produce and consume energy. It offers a clean and renewable source of fuel that can be used in a variety of applications, from transportation to power generation. However, the widespread adoption of hydrogen technology still faces some major challenges, such as the high cost of production and distribution infrastructure. Despite these challenges, many countries and companies are investing heavily in the development and deployment of hydrogen technology, and it is likely that we will see significant progress in this field in the coming years. As we move towards a more sustainable future, hydrogen technology is a promising solution that could play a critical role in reducing greenhouse gas emissions and mitigating the impacts of climate change.

While the energy density of hydrogen by weight is high, its volumetric energy density is relatively low compared to other fuels, including gasoline and diesel. This is because hydrogen has a very low density at standard temperature and pressure (STP) and needs to be stored under high pressure or at very low temperatures to achieve sufficient energy density. This means that storing the same amount of energy in hydrogen as in gasoline or diesel requires much larger storage volumes.

The low volumetric energy density of hydrogen is a disadvantage for certain applications, particularly in transportation, where space is limited and weight is a critical factor. It also presents challenges for the storage and distribution of hydrogen, as larger tanks or pipelines are required to store and transport the same amount of energy as other fuels. To overcome this disadvantage, researchers are exploring new storage and distribution methods, such as using materials that can absorb hydrogen at low pressures or developing more efficient compression and liquefaction technologies. These advances could help to improve the volumetric energy density of hydrogen and make it a more practical option for a wider range of applications.

UHS offers a way to store excess renewable energy and make it available when needed, thereby addressing one of the major challenges of renewable energy sources. However, there are several challenges that must be addressed to ensure the widespread adoption of UHS. Researchers extensively studying two types of geological settings for UHS: salt caverns and porous reservoir rocks (including depleted oil/gas fields and aquifers). Currently, the technology for storing hydrogen in salt caverns is in an advanced stage, with four commercial-scale projects worldwide: one in the United Kingdom (Teeside) and three in the United States (Clemens, Moss Bluff, and Spindletop). Salt caverns offer advantages such as fracture prevention due to the plastic behaviour of salt and minimal microbial activity in extreme brine conditions, ensuring the purity of hydrogen. However, their volume is limited compared to aquifers/depleted reservoirs, and operating at greater depths can be challenging due to the rheological properties of salt.

Energy security necessitates large-volume storage solutions, leading researchers to also focus on porous reservoirs. However, there are currently very few pilot projects worldwide to validate their applicability, with examples being the pilot project from RAG Austria and the Hychico project in Argentina. Field-specific hydrodynamical behavior of hydrogen raises concerns, including possible gas losses due to water presence, biological/chemical reactions, and dissolution. Viscous fingering and methanation are widely mentioned in the literature as potential causes of hydrogen loss, emphasizing the need for field-specific observations. Additionally, studying corrosion, steel embrittlement, and hydrogen reactivity with surface facilities is crucial. Cost and public acceptance are significant factors hindering the rapid advancement of the hydrogen economy. Addressing these challenges is essential for the successful integration and widespread adoption of hydrogen as an energy carrier.

Section 7 briefs about the old gas and oil fields in Hessen, discovered in the mid-20th century in the Upper Rhine Graben. Notably, Stockstadt and Hähnlein, developed for gas storage, have favorable reservoir properties. Wolfskehlen, structurally related to Stockstadt, presents similar reservoir dimensions and properties. Abandoned fields like Darmstadt and Pfungstadt offer potential. The acquired 3D seismic data aids prospect identification, and operational data for Underground Gas Storage (UGS) is accessible. Feasibility studies explore hydrogen storage and in-situ methanation possibilities. These fields meet criteria for exploration—suitable geological settings, existing infrastructure, and data availability—positioning them as promising candidates for energy storage and hydrogen utilization.

The development of national hydrogen strategies by some of the world's largest economies is a significant step towards achieving a more sustainable energy system. The strategies outline ambitious targets for the production and use of hydrogen, as well as the necessary infrastructure investments to support this growth. However, the success of these strategies will depend on a number of factors, including the availability of low-cost renewable energy to power hydrogen production and the development of efficient and safe methods of storing and transporting hydrogen.

Furthermore, it will be important for these countries to collaborate on the development and deployment of hydrogen technology to ensure that it is accessible to all and can be deployed at scale. Overall, the national hydrogen strategies represent a significant opportunity to accelerate the transition to a more sustainable energy system and address one of the most pressing challenges of our time.

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Appendices

A. Graphs

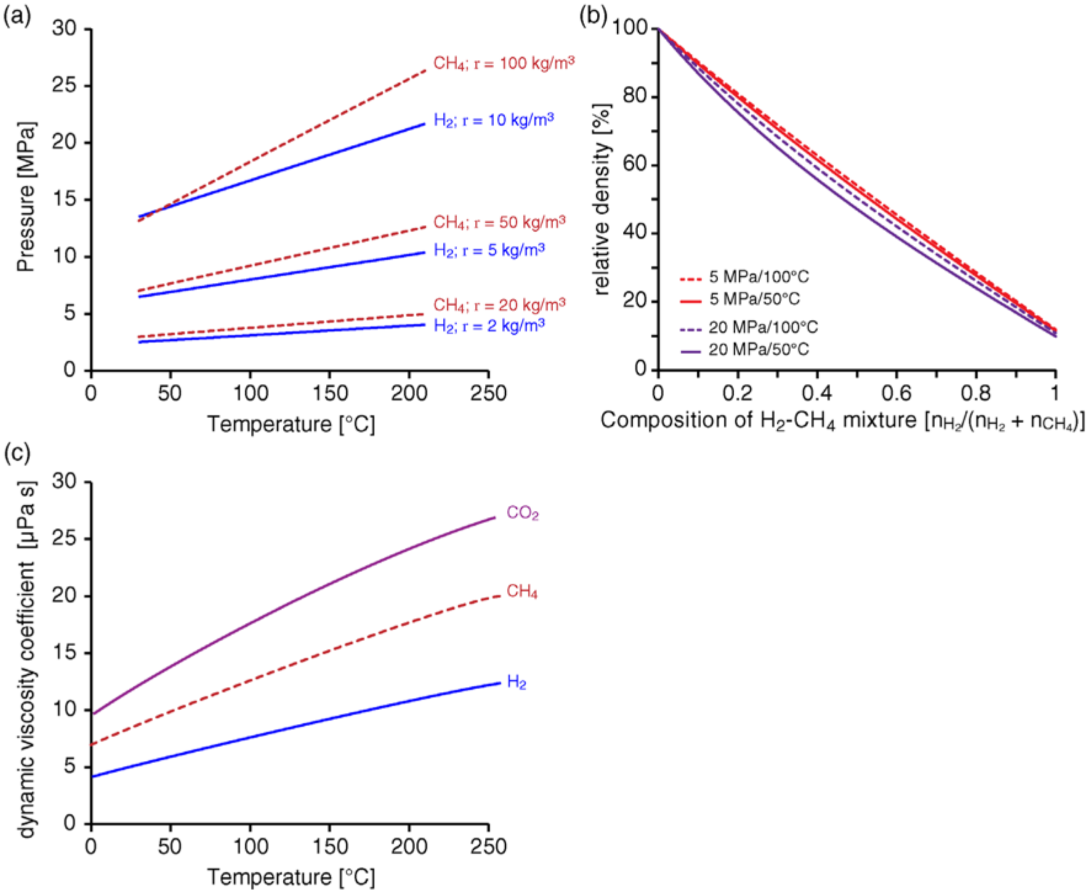

Figure 32: Comparison of the density of hydrogen and methane (a) and density of hydrogen-methane gas mixtures (b) as calculated with the GERG 2004 XT08 EOS (refer[29] for original citation). (c) Temperature dependency of the coefficient of dynamic viscosity of H_2 , CH_4 and CO_2 (for comparison) at atmospheric pressure, modified after Reference[45] by Liebscher et al.[29]

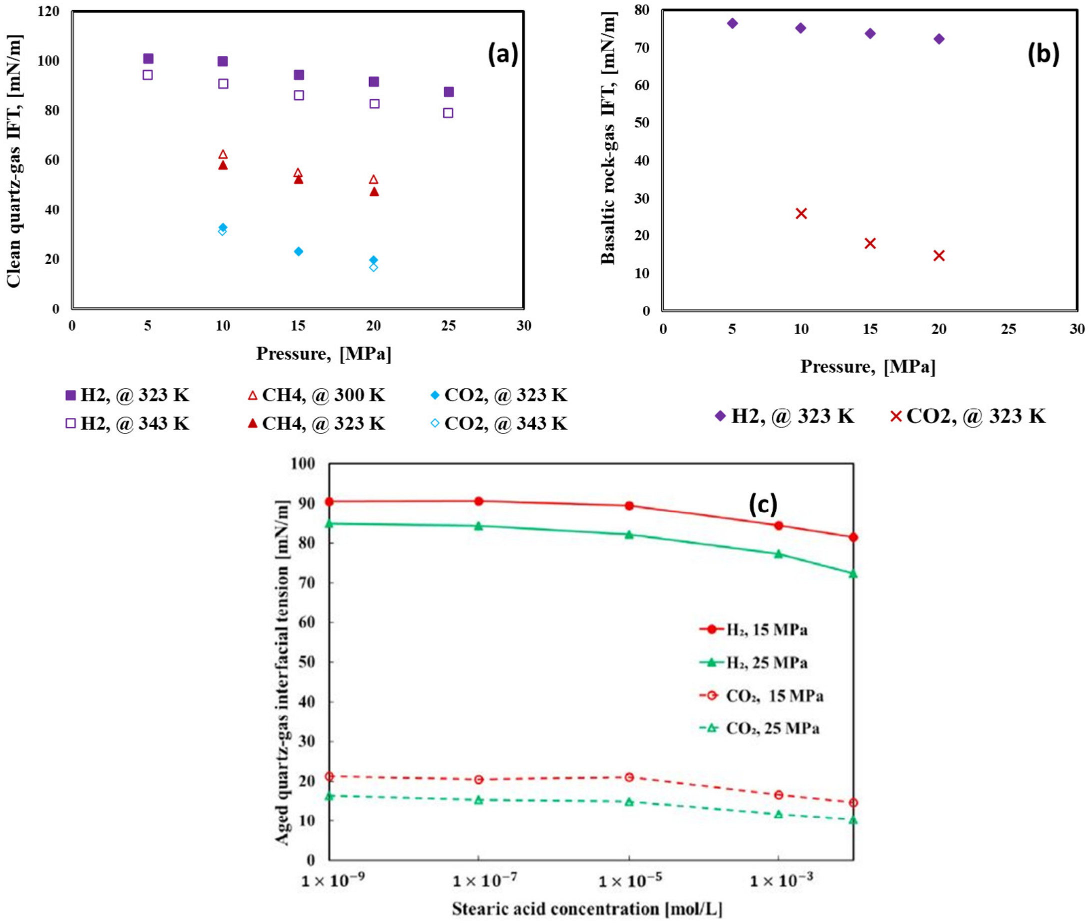

Figure 33: Rock–gas IFT for (a) clean quartz and (b) basaltic rock, against pressure; and (c) aged quartz gas-IFT against concentration, at 323 K. Source: Data obtained from Pan et al. (2021b). For original data source refer[43].

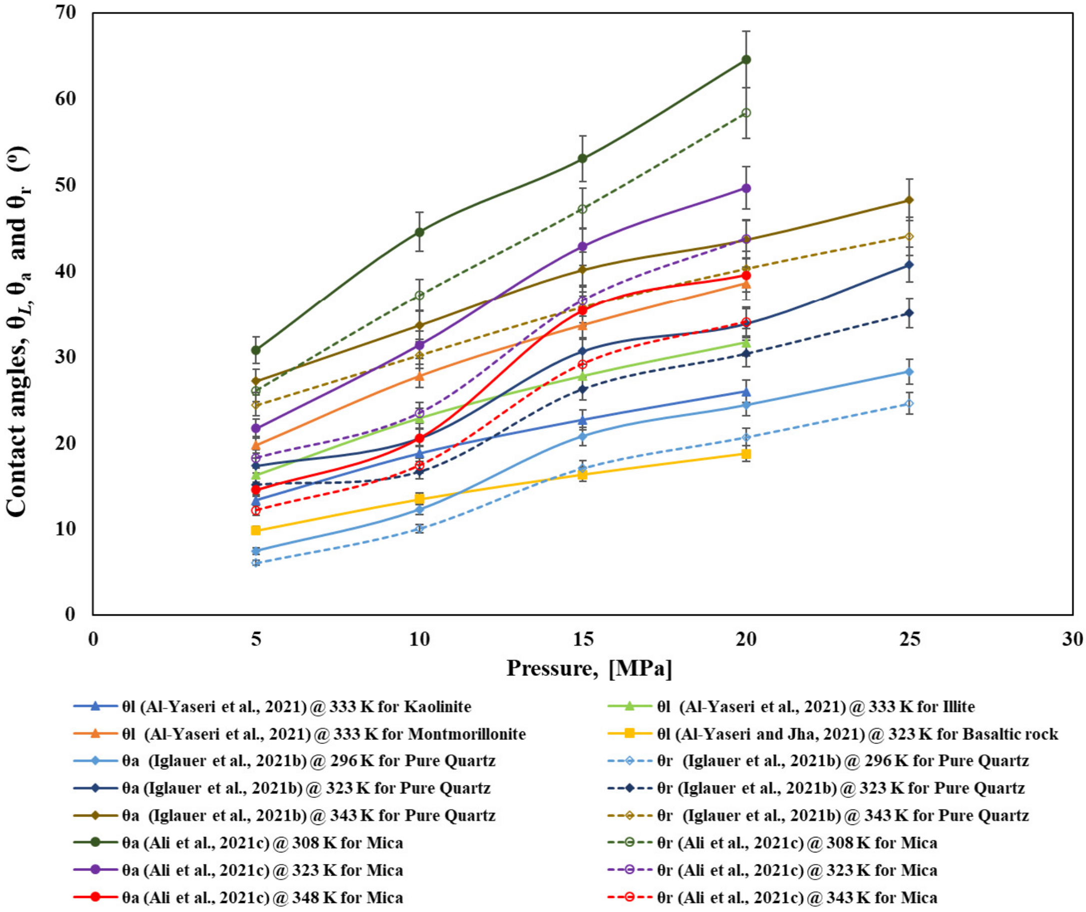

Figure 34: Experimental data for rock/brine/H_2 at different conditions. Data compiled by Muhammed et al.[43]. For original data source refer[43].

B. Bibliography category wise

Table 17: Current literature summary related to UHS modeling modified after Muhammed et al.[43], refer the review paper by Muhammed et al.[43] for corresponding references.

Author(s)	Objectives	Software tool(s)	Storage duration	Storage medium	Injected gas	Adopted approach(s)	Major findings
Pfeiffer and Bauer (2015)	Investigated the hypothetical behavior of subsurface porous media H_2 storage site using numerical simulation	Eclipse 300	Short term	Existing Rhaetian anticlinal structure based on saline aquifer model	N_2 and H_2	- Peng–Robinson EOS for property modeling	- Simulation shows that storage can supply about 20% demand for electrical energy for 1 week - An optimized injection scheme can further improve the storage performance
Hagemann et al. (2015)	Mathematical modeling of unstable transport (gas rising, lateral spreading, and hydrodynamics) in UHS	Open-source code DuMu^x	Short term	Aquifer	H_2 and CH_4	- Selective technology - Darcy's law - Brooks Corey - Box-method	- Injection rate controls gravitational and viscosity forces displacements - Gas rise and leakage is delayed by storing H2 in a stratified manner through selective technology - The lateral extent of the barriers significantly influence gas rising and also depends on gas type
Amid et al. (2016)	Seasonal storage of H_2 by comparing the respective capacities and deliverability in a UK storage facility	PHREEQC (geochemical modeling)	Short term	Depleted gas	H_2	- Volumetric analysis - Chemical stability study - Leakage study	- The facility could store about 42% of the energy capacity supplied - H2 loss due to dissolution and diffusion could be reduced to < 0.1%
Feldmann et al. (2016)	Investigated the effect of gas mixing, seasonal injection and production cycles, and hydrodynamics of UHS	Open-source code DuMu^x (flow transport process) and COMSOL Multiphysics (numerically simulate gas displacement front)	Long term	Depleted gas	H_2, CO_2, CH_4, and H_2O	- Peaceman's model - Selective technology - conventional cell-centered finite volume method - Molecular diffusion - Mechanical dispersion	- Good UHS potential - H2 storage in stratified aquifers limits gas loss due to lateral spreading or viscous fingering beyond the spill point - Selective technology implementation is considered a good way of H2 production - Native fluid displacement efficiency depends on the extent of gravity override and viscous fingering
Pfeiffer et al. (2016)	Numerical simulation and geophysical monitoring of a synthetic, heterogeneous field site for UHS	Eclipse 300	Short term	Existing Rhaetian anticlinal structure based on Saline aquifer model	H_2 and N_2	- Peng-Robinson EOS - gravity modeling - facies modeling - P-wave velocity - petrophysical rock model - Gassmann fluid substitution model - seismic mapping, flow simulation model - geoelectric resistivity model	- H2 storage was found to increase with cycle numbers as more H2 was available at the final storage cycle - Detailed multi-dimensional information for UHS was presented in this study
Hagemann et al. (2016)	Studied the effect of H2 hydrodynamics for effective comparison between natural gas and depleted gas reservoir	Open-source code DuMu^x	-	Depleted gas	H_2 and CH_4	- Darcy's law - Fick's law - Brooks Corey - Mathematical - Hydro-dynamical model	- The importance of injection rate was emphasized, and it showed that a high injection rate leads to an unstable and lateral finger spreading below the caprock - Observed that lateral fingers are more pronounced in UHS than in storage of natural gas
Pfeiffer et al. (2017)	H2 storage in heterogeneous sandstone effects of dimensioning and induced hydraulics	Eclipse 300	Short term	Existing Rhaetian anticlinal structure based on Saline aquifer model	H_2 and N_2	- Peng-Robinson EOS - facies modeling	- Storage is mainly limited by the achievable extraction rates. - This study provides detailed information on how heterogeneous parameter distribution affects storage efficiency

Sainz-Garcia et al. (2017)	Assessment of feasible strategies for seasonal underground H2 storage	COMSOL Multiphysics	Long term	Saline aquifer	H_2 + CH_4	- 3D multiphase model - Darcy's law - Brooks Corey	- A maximum H_2 recovery ratio of 78%, was achieved - No viscous fingering - Steeply dipping structures can store H_2 gas without cushion gas, though it is prone to up coning - H_2 is best recovered if several shallow extraction wells are located beneath the caprock
Pfeiffer and Bauer (2018)	To compare simulations of H2 storage in a sandstone formation using heterogeneous and homogeneous flow property models	Eclipse 300	Short term	Existing Rhaetian anticlinal structure based on Saline aquifer model	H_2 and N_2	- Analytical averaging methods	- This study can provide detailed multi-dimensional information on the applicability of spatial averaging methods for approximating storage characteristics
Hemme and Berk (2018)	To identify potential risks during storage	PHREEQC (geochemical modeling)	Long term	Depleted gas	H_2	- one-dimensional reactive mass transport (1DRMT) - Monod model	- Observed losses due to diffusion through the cap rock - Storage time, pressure, temperature, kinetic rate, and stored gas composition significantly influence the overall loss
Hassannayebi et al. (2019)	Multi-step geochemical study of fluid-rock interactions using equilibrium and kinetic batch simulations in Molasse basin, Upper Austria	Geochemist workbench (GWB)	Short and long term	Depleted gas	H_2 + CH_4 mixture	- Equilibrium modeling - Primary kinetic batch modeling - Final kinetic batch modeling	- The kinetic batch model shows that H_2 interactions with minerals require time scales much larger than a typical H_2 storage cycle - Interactions among H_2 and brine components are recognized to be more relevant within the storage cycle of H_2 - Observed pyrite reduction into pyrrhotite significantly increased the reservoir pH and further led to H_2-loss.
Luboń and Tarkowski (2020)	Evaluation of the viability of seasonal (cyclic) H_2 storage	PetraSim-TOUGH2	Long term	Aquifer	H_2	- Isothermal assumption - Multi-phase flow modeling - Geothermal modeling	- Up coning was reported as the major issue in the aquifer - The percentage recovery of H_2 increased with withdrawal cycles - Water management is considered a potential environmental challenge
Lysyy et al. (2021)	Seasonal H_2 storage evaluation	Eclipse 100	Long term	Depleted oil and gas field	H_2 and CH_4	- History matching - Storage initialization - Cyclic operation - Prolonged withdrawal investigation Case studies	- Annual H_2 delivery of 400 million Sm3 was achieved - 87% of H_2 was recovered - Injection of 30% H_2 with gas mixture resulted in fluctuation in H_2 delivery - Dipping structure was considered as not a good H_2 storage candidate
Heinemann et al. (2021b)	A comprehensive investigation on the role of cushion gas for H_2 injection and production	Petrel GEM	Long term	Depleted gas	H_2	- One injection and production well assumption - SRK EOS used H_2 property modeling - Peaceman's model was used in GEM for reservoir flow rate	- Cushion gas is an important component for exploiting the total capacity of an H_2 storage site - Cushion gas to working gas capacity depends on geological parameters including storage reservoir depth, anticline structure, and reservoir permeability
Delshad et al. (2022)	Hydrogen Storage Assessment in Depleted Oil Reservoir and Saline Aquifer	CMG-GEM	Long term	Depleted oil field Saline aquifer	H_2	- One injection and production well assumption - SRK EOS used H_2 property modeling - Peaceman's model was used in GEM for reservoir flow rate	- Cushion gas is an important component for exploiting the total capacity of an H_2 storage site - Cushion gas to working gas capacity depends on geological parameters including storage reservoir depth, anticline structure, and reservoir permeability