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Large Hydrogen Underground Storage

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About Roads2HyCom

Roads2HyCom is a project supported by the European Commission's Framework Six program. Its purpose is to assess and monitor hydrogen and fuel cell technologies for stationary and mobile energy applications.This is done by considering what the technology is capable of, relative to current and future hydrogen infrastructures and energy resources, and the needs of communities that may be early adopters of the technology.By doing this, the project will support the Commission and stakeholders in planning future research activities. Project main website: http://www.roads2hy.com

HyLights, Roads2HyCom and the Hydrogen and Fuel Cells Technology Platform (HFP)

The European Commission is supporting the Coordination Action "HyLights" and the Integrated Project "Roads2HyCom" in the field of Hydrogen and Fuel Cells. The two projects support the Commission in the monitoring and coordination of ongoing activities of the HFP, and provide input to the HFP for the planning and preparation of future research and demonstration activities within an integrated EU strategy.

The two projects are complementary and are working in close coordination. HyLights focuses on the preparation of the large scale demonstration for transport applications, while Roads2Hycom focuses on identifying opportunities for research activities relative to the needs of industrial stakeholders and Hydrogen Communities that could contribute to the early adoption of hydrogen as a universal energy vector. Further information on HyLights is available on the project web-site at http://www.hylights.org.

Contents

Introduction

The storage of large quantities of hydrogen underground is a key step for the hydrogen economy. One can store hydrogen as either a gas or a liquid. Both approaches are examined hereafter and appear to be already at an industrial level. The stakes of these sector is to keep the cost of such operation as low as possible and to avoid as much as possible leaks of hydrogen.

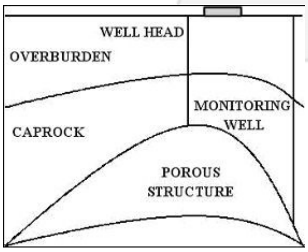
The most widely studied options for storing large quantities of gaseous hydrogen are underground depleted gas fields or aquifers, and caverns. This will be analyzed in the first section below. Then underground storage in buried tanks, either in compressed gas form or in liquid form will be illustrated by a few examples in the second section. Eventually the economical aspects of each technological option will also be examined.

State of the Art

Large Scale Underground Hydrogen Storage

Natural gas bas been stored underground since 1916 and much of the experience is directly applicable to hydrogen. Originally underground storage was confined to depleted oil and gas fields. They are porous rock structures not unlike those associated with aquifers. Such storage facilities tend to be extremely large; volumes of gas stored exceed 10^9 Nm^3. Pressures can be up to 40 atm. As illustrated in the figure below, any underground storage in porous media requires the following features :

- a stratum of porous rock, usually sand or sandstone, at a depth of 150 - 900 m below the surface ;
- an impervious caprock of adequate thickness ;
- a suitable geological structure such as an anticline, which usually forms a dome-shaped geologic structure.



Schematics of a depleted fossil oil or gas well, or aquifer. From Stone et al (2005)

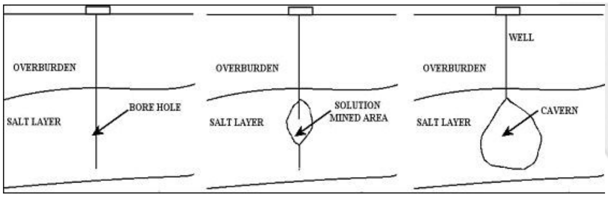
The porosity of the sandstone or sand must be sufficiently high to provide a reasonable void place in an aggregate sense to yield an economically acceptable storage volume. The permeability must be high enough to provide an adequate rate of inlet flow (injection) and outlet transmission injection (withdrawal). On the other hand, the caprock structure must be reasonably impermeable if it is to contain the gas.

During exploitation one needs to maintain a minimum base gas or "cushion gas" which is the volume of gas intended as permanent inventory in the storage reservoir to maintain adequate pressure and deliverability rates throughout the withdrawal season. In the case of hydrogen storage it has been proposed to use a cushion gas of different nature, such as natural gas, to displace a hydrogen-rich gas (Paterson, 1983). But this is valid only if gas stratification can be maintained between cushion gas and hydrogen by avoiding interdiffusion or "fingering". Nevertheless this would also require an efficient gas separator (membrane or PSA) in the gas station at ground level.

An important point to note regarding the performance of the caprock structure is the mechanism involved in sealing the top of the underground reservoir, either a depleted field or an aquifer. This sealing occurs because of water capillary action, in which water fills all the voids of the caprock structure and must be expelled by sufficiently high pressure to overcome the capillary resistances (the threshold pressure of the caprock). Below this incremental pressure, the caprock will act as an effective barrier to the passage of any gas. This incremental or threshold pressure and the effectiveness of the sealing action is independent of the nature of the gas because it is a water-rock capillary effect. This is an important observation in that it indicates that hydrogen in underground storage will behave much like natural gas insofar as integrity against leakage is concerned.

The scientific treatment of the dynamics of gas transfer in such porous media consists in solving thermodynamic and transport equations using appropriate equation of states for the gas or gas mixtures and diffusion -permeation due to a pressure gradient according to Darcy's law to derive the gas extraction rate (Stone *et al* 2005). Moreover Panfilov *et al* (2006) have recently studied and modelled a curious physical-chemical phenomenon which can affect underground storage of H_2 CO_2-CH_4 mixtures. It is characterized by a reduction in H_2 and CO_2 concentrations, concomittant with an increase of the CH_4 fraction. These phenomena were observed in the Lobodice and in the Beynes town gas storages where the original stored mixture of 55% H_2, 20% CO_2+CO and 20% CH_4 was transformed into a new gas containing 37% H_2, 12% CO_2+CO and 40% CH_4. Simultaneously a small reduction in the total gas volume (~15%) was observed. These results are ascribed to two chemical reactions CO_2+4H_2 ® CH_4 +H_2O and CO+$3H_2$ ® CH_4+H_2O induced by micro-organisms (methanogenic bacteria) present in stratal water within porous rocks.

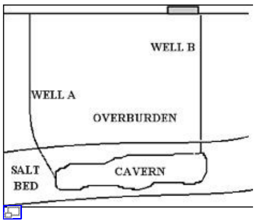
Where previously mined cavities are available which are, or can be made, gas tight, there is an opportunity to use these as artificial underground structures for hydrogen storage. A special case is the use of solution-mined salt caverns as illustrated in the figure below.



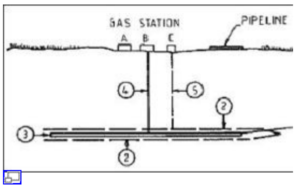
Schematics of the solution-mining of a salt cavern : a) initial bore hole, b) solution mining in process c) final solution-mined cavern. From Stone et al (2005)

In locations where the salt layer is between 60 to 100 metres thick it is debatable whether a vertically mined salt cavern could be used to store the required volume of hydrogen. In such locations horizontal drilling with solution mining techniques (refer figure) will be preferred unless a collection of smaller vertical solution mined caverns could be inter-connected (Stone *et al*, 2005). Alternatively caverns can be drilled in rocks. Lindblom (1985) made a detailed study a conceptual design for compressed hydrogen storage in mined rock caverns consisting of parallel tunnels surrounded by a water curtain as illustrated in the figure.

Unlike depleted field and aquifer storage systems, cavern storage involves large open, void spaces to be filled with gas. A more complex structural analysis is therefore required to establish feasibility. For example, if the pressure in the cavity is allowed to drop significantly below ambient pressure, a collapsing stress situation is created which might result in loss of structural integrity of the storage volume. One approach considered is to replace the gas drawn off with water so that the cavity pressure is maintained. There is of course no cushion gas requirement in this hydraulically compensated scheme and the delivery pressure is constant equivalent to the hydraulic head. The disadvantage for storage in salt caveras is that the working fluid must be saturated brine. Surface storage of this is complicated by many environmental constraints.



Schematics of an horizontal solution-mined salt cavern. From Stone et al (2005)



Concept of a compressed hydrogen storage cavern consisting of parallel tunnels drilled in the rock and surrounded by a water curtain. From Lindblom (1985)

Recently, Morrow *et al* (2006) of Praxair Technology Inc. have patented a method of hydrogen underground storage in a salt cavern and the subsequent reinjection into a pipeline after different compression, extraction and purification steps.

Single salt caverns can be 50 10^6 m^3, whereas hard rock caverns would be one tenth of this size. However, modern mining machinery and techniques make the costs of mined caverns comparable to other underground options. In the Lindblom rock-cavern concept the water curtain system has three important fonctions: i) to maintain water saturation in the rock fracture system during excavation of the cavern, ii) to regulate the pressure difference between water and gas as to ensure that gas breakthrough is impossible, iii) to induce an artificially high water pressure around the cavern as to make the use of higher gas pressure possible.

Buried Tanks

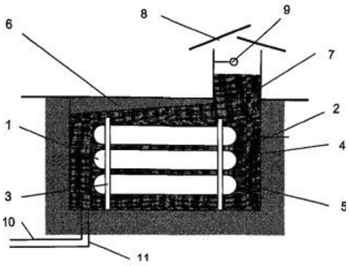
Underground storage may also consist in burying compressed gas or liquid hydrogen tanks that are usually placed at ground level, in order to save ground space. Of course this option should only apply for smaller hydrogen quantities (typically 10^3 to 10^4 Nm^3) and at a much smaller depth (typically a few meters) than direct gas storage in caverns.

Nevertheless the challenge of local storage of hydrogen in future hydrogen vehicle refuelling stations has triggered a new interest and proposals for this option. Indeed when referring to the largest existing gasoline fueling stations in Europe - which are scaled to refill several hundreds up to one thousand cars per day with a local storage capacity corresponding to two days of consumption - the equivalent hydrogen refueling stations in the future should be able to store up to 10 tons of hydrogen. This corresponds to a volume of the order of several 10^5 Nm^3, or 250 m^3 at 700 bars, or 140 m^3 of LH_2 !

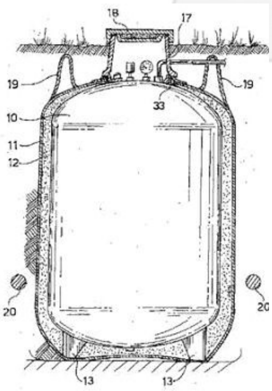
Compressed Gas Tanks

Presently the largest manufactured compressed hydrogen tanks in the world (about 15000 m^3) can be pressurized only up to 12-16 bar. Individual metallic cylindrical tanks at 200-300 bar can be scaled up to ~ 1000 liters (inner water volume) each for hydrogen transport in tube trailers where currently about 15 tubes are bundled together.

Large volume high pressure gas tanks made of carbon fiber-reinforced composite vessels are presently developed for CNG or H_2 by a few companies.



Underground compressed gas storage in pressure vessels (1) immersed in a basin (4) filled with a liquid (5), with interconnecting piping and connections (2), an anchoring system (3), a cover with a slanted surface on the underside (6) for covering the basin and leading any gas leak towards and through a vent (7), with a gas detection equipment (9) protecte with a light cover (8). The basin can be filled an emptied with an appropriate water piping (10 and 11) . From Schelling *et al* (2006)



Gas tank with protection system for underground installation. From Poillucci (2003)

Although a compressed gas storage installation is usually place outdoor, on or above ground level, it can be buried to save ground space and also to provide improved protection from external influences such as radiation from adjacent fires or damage caused by explosions. However this alternative is rarely used because as it makes inspection of the vessels and interconnection of pipes less easy, and it requires preventive measure to prevent corrosion. Nevertheless to overcome the difficulty of inspection and pipe interconnection it has been proposed to place the tanks in a basin and submerge them afterward with a liquid such as water, so that tank protection from heating and and explosion is compatible with an easy inspection simply by lowering the water level in the basin. Leak detection could be an issue but some solutions exist such as the one proposed by Norsk Hydro (Schelling *et al* 2006) and illustrated in the figure. Alternatively the tank can be placed in a protection system consisting of a sack that contains the tank and a gas permeable material arranged in such a manner as to constitute a layer around the tank (Poillucci, 2003). The sack can be material impermeable to water and gas as shown in the figure above.

Liquid Tanks

At present the technology of liquid hydrogen (LH_2) storage is state-of-the-art thanks to extensive applications in space propulsion. LH_2 tanks for long time storage have double vacuum perlit vacuum insulation. Common stationary tanks have capacities ranging from 1500 liters (approx. 1100 Nm^3 or 100 kg H_2) up to 75000 liters (~ 60000 Nm^3 or ~5 tons of H_2) with radii of 1.4 m to 3.8 m and heights from 3 m up to 14 m. Since the hydrogen liquefaction capacity in North America is ten times larger than in Europe (300 tons/day in 2004 in North America, including 224 tons/day in the USA, versus 20 tons/day in Europe) there are more of such tanks in the USA, the largest of which belongs to NASA and is located at Cape Canaveral. This tank, at ground level, has a storage volume of about 3800 m^3 (~ 270 tons LH_2). With an outer spherical diameter of 20 m, its evaporation rate is under 0.03% per day, allowing for a storage period of several years. As compared with pressurized gas storage, this method offers more inexpensive storage costs when dealing with large quantities. The energy required for liquefaction may not be a barrier if the hydrogen is to be transported as a liquid anyway, or if the end-use application requires its fuel to be in liquid form.

The benefits of underground LH_2 stationary storage can be summarized as follows: i) it decreased land usage and footprint, ii) reduced potential hazards (vandalism, fire, vehicle impact), iii) inherent spill containment. Actually this underground storage solution has been also considered for LNG storage.

Currently there are only a few examples of LH_2 tank being either placed in a room underground or actually buried underground.

Main metrics

METRIC	SUB-METRIC	DATA / RATING	UNITS	Compressed Underground Hydrogen	Liquid Hydrogen
Technology Accessibility	Compatibility with existing technologies	Rating	0-4	4	4
	Number of retailers & depots	Data	number	N/A	N/A
	Space available at retailers and depots	Rating	0-4	N/A	N/A
Global Environmental Impact (to be coordinated	GHG emissions associated with fuel retail and depot	Data	gCO2 eq / kg fuel	0	0
		Data		0	0

with ECN)	CO2 emissions associated with fuel production		gCO2 / kg fuel		
Local Environmental Impact (to be coordinated with ECN)	Air quality impact (consider NOx, PM, CO, NMHC)	Rating	0-4		
	Noise or perception of noise from retail and depot (SPL,loudness...)	Data/Rating	dB(A), sone		
	Land use / damage to nature (eg. fuel depots)	Rating	0-4		
Efficiency	Global energy efficiency	Data	%	N/A	N/A
	Energy efficiency of auxiliary facilities	Data	%	N/A	N/A
Capacity & Availability (to be coordinated with ECN)	Measured capacity of retailers and depots	Data	kg fuel / facility	up to 1 000 000 000 nm3	1 00 000 nm3
	Availability of retailers and depots	Data	%		
	Lifetime of technology	Data	years	?	?
Safety (to be coordinated with TNO)	Leaks at retail or depot per number of tanks	Data	no. / year		
	Severity of failure	Rating	0-4		

Market / Diffusion

Underground Hydrogen Storage

Basically there are four underground formations in which gas can be stored under pressure:

- Depleted oil or gas fields,
- Aquifers,
- Excavated rock caverns or mines,
- Solution-mined salt caverns.

For example, there are already twenty-three salt caverns being used for natural gas or hydrogen storage in the UK. These are located in Cheshire, in Stafford and in Yorkshire. There are also another twenty-four salt caverns planned for natural gas storage (Stone *et al*, 2005). In France there are at least fifteen underground storage sites for natural gas, either in salt caverns or in aquifers, for total useful capacity of 110 TWh, i.e. about 30% of the present annual consumption.

Underground storage of hydrogen and synthetic gas (H_2-CO) mixes is not a new concept. A major study of underground storage of gaseous hydrogen was conducted in 1979 by the Institute of Gas Technology (now known as Gas Technology Institute, GTI) in the USA (Foh *et al* 1979). Over the last decades there have been several examples of underground storage of pure hydrogen or synthetic gas H_2-CO mixtures (Panfilov 2006) :

- In England, at Teesside, Yorkshire, the British company ICI has stored 1 million Nm^3 of nearly pure hydrogen (95% of H_2 and 3-4% of CO_2) in three salt caverns at about 400 m in depth for a number of years.
- In France, at Beynes, Ile de France, the gas company Gaz de France has stored a synthetic "town gas" 50-60% hydrogen in an aquifer of 330 million Nm^3 capacity between 1956 and 1974 . No gas losses or safety problems have been reported
- In Russia, pure hydrogen was stored underground at 90 bars for the needs of the aerospace industry
- In Germany, at Kiel, a 62% H_2 town gas was stored in a salt cavern of 32000 m^3 at 80-100 bar
- In Czechoslovakia, at Lobodice a 50% H_2 town gas was stored in an aquifer.

Praxair is presently constructing a large underground hydrogen storage facility to enable "peak shaving" of its hydrogen production. This facility, located in Texas, will utilize a salt cavern, and will be the first of its kind in the industrial gases industry. Connected to the Praxair?s hydrogen pipeline network which serves large in Texas and Louisiana it will significantly increase the on-demand availability of hydrogen during periods of peak demand. This peak-shaving system should be brought on line in 2007.

The report of the 1979 study by the Institute of Gas Technology (Foh *et al* 1979) confirmed the economic and technical feasibility of large-scale underground hydrogen storage. According to Taylor *et al* (1986) underground storage is the most inexpensive mean of storing large quantities of gaseous hydrogen. Indeed underground hydrogen gas storage is about two orders of magnitude cheaper than tank storage when applied to volumes of several million Nm^3 of hydrogen. The lower capital investment is in salt caverns, and the highest for depleted gas wells.

In depleted gas wells the gas stored in a field is divided into active working gas and cushion gas. The latter is an inactive base gas not recoverable, and it can be considered as an investment or a minimum inventory. The ratio of working to cushion gas varies widely with a ratio greater than 2:1 generally being preferred. As hydrogen is relatively expensive commodity, the cost of the cushion gas is a very significant part of the capital charges for such large storage reservoirs. However, as the cavern is repeatedly cycled, the initial cushion gas cost is amortized (Stone et al, 2005).

Mining a salt-cavern may take a year or more to mine, which accounts for 25% to 35% of the total initial investment (Stone *et al* 2005). In his study of a conceptual hydrogen storage cavern of 300 million m^3 at 650 m depth in competent rock, Lindblow (1985) estimated a three and half year time break-down for construction and a total cost of U.S .$39-64 million which should exceed $100 millions by now. From this we can estimate an investment cost ratio of about 0.3 ¤ per H_2 Nm^3.

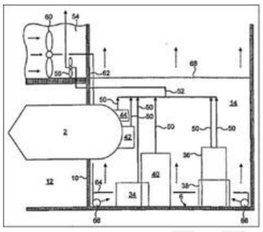
Buried Tanks

Compress Hydrogen

There are actually no industrial solution for large hydrogen compressed tanks and this type of solution is still under developpement. For example Lincoln Composites has already manufactured type IV vessels with plastic liner at 7000 psi (483 bar) for small size hydrogen refuelling stations (50kgH_2/day); the company is presently working on a new tank with plastic liner at 5000 psi (350 bar), approximately 1.08 meter diameter by 11.5 meters length, with a storage volume of approximately 8700 liters (water volume).

Buried compressed gas tanks are relevant only for small quantities, from 100 to 1000 kg of H_2 (~ 1000 to 10000 Nm^3), and their cost, including excavation and basement installation is obviously much larger, in the range of 10 to 100 EUR per Nm^3.

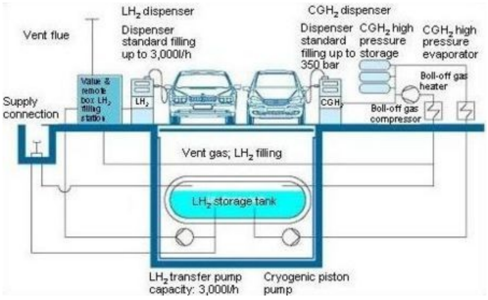
Liquid Hydrogen




Underground storage for the LH2 tank in the BP hydrogen refuelling station located in London. The picture of the tank is from Cryolor (tank manufacturer, subsidiary of Air Liquide), and the schematic drawing of the installation is taken from Roach (2004)

The first example of LH_2 tank was operated for the bus refuelling station of BP in London within the HyFleet-CUTE project. The cryogenic tank of liters capacity (tons of LH_2), manufactured by Air Liquide for BOC, is placed in a basement, with a technical room for operators separated from the main body of the tank for safety reasons (Roach 2004), as illustrated in figure.

The second example is the concept proposed by Linde (Trill and Wolf, 2006) for future hydrogen filling stations offering both LH_2 and CGH_2, as illustrated in figure below. This concept of underground LH_2 storage will soon be applied in the construction of a hydrogen refuelling station for BMW in Münich in 2007.



Linde concept for future hydrogen filling stations for GH_2 and LH_2 with underground storage tanks.
Eventually the third example is the concept proposed and developed by Air Products for the Shell Hydrogen refuelling station in Washington DC, as illustrated in the figure. The originality of this solution is all connections are accessible at ground level after the tank has been vertically slided in a cylindrical cavity. This concept applies for storage volumes from 1500 up to 9000 gallons (~ 400 up ~ 2400 liters) of LH_2, equivalent to 27 - 167 kg, or 320 - 1920 Nm^3 of H_2, and the boil off rate is less than 0.5% per day.

Air Products' underground LH_2 tank being installed at the Shell Hydrogen refuelling station in Washington DC in 2004.

Main industrial players

The main industrial players for large hydrogen storage systems are actually the major international companies that are selling industrial gases namaly Praxair, Air Products, BOC, Linde, or l'Air Liquide.

The research and development projects are mainly focused on reducing cost and hydrogen leaks. Safety can also be an issue.

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