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Enabling Large-Scale Hydrogen Storage in Salt Caverns:

Recent Developments

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ENABLING LARGE-SCALE HYDROGEN STORAGE IN SALT CAVERNS: RECENT DEVELOPMENTS

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Abstract

Storing pure hydrogen in salt caverns has been practiced since the 70's in Europe, only a decade after the first natural gas storage in salt cavern was commissioned in the USA. Despite this long experience, the recent plan for hydrogen as a pillar of a future low carbon energy system has intensified the focus on hydrogen storage and prompted significant research work. It has led to technical or scientific developments in fields that were poorly understood until recently.

This article presents a high-level overview of the recent developments to the current knowledge or industrial practice for hydrogen storage in underground salt caverns. Developments regarding specificities of hydrogen towards the rock salt or brine will be presented: rock salt permeability to hydrogen, hydrogen thermodynamics and solubility in saturated brine. Adaptation of MITs will be discussed. Geochemistry reactions and risk management of the microbiological activity in the brine in presence of hydrogen will be tackled. Last, materials compatibility with H₂ due to its small size will be reviewed and especially the compatibility with steel and elastomer for cavern wells.

This article is an opportunity to present the recent developments that have been done regarding hydrogen storage in salt caverns, but also to discuss the technical challenges that our industry still have to overcome due notably to the lack of standards for well design and well equipment.

Key words: Hydrogen Storage in Salt Caverns, Material Compatibility, Rock Salt Permeability, Hydrogen Solubility, Geochemistry with Hydrogen

1. Introduction

1.1. Historical Experience in Hydrogen Storage in salt caverns

Hydrogen technologies is anticipated to be one of the pillars of future energy and transport systems, making a valued contribution to the transformation to a low carbon economy. Renewable hydrogen, when combined with large scale underground storage in aguifers, depleted fields, or salt caverns, enables transportation of energy through time, balancing out the impacts of variable energy production from renewable energy sources.

Storing pure hydrogen in salt caverns has been practiced since the 70's in Europe, only a decade after the first gas storage in underground salt caverns started (a natural gas storage in the USA). Six (6) caverns are operating today, as presented in the figure below (next page).



Figure 1: Salt caverns storing pure, or nearly pure, hydrogen in operation and their main characteristics. Information from various sources, most notably Bérest et al. (2021).

In addition to this experience of underground storage of hydrogen in six (6) salt caverns, complementary industrial experience comes from underground town gas storage. There is a historical experience of storing blends of hydrogen and other gases: in the 19th Century and the first half of the 20th Century, so called "town gas" or "manufactured gas" was used for heating and cooking until its replacement by natural gas. It typically contained 30%–50% hydrogen and has been stored in six (6) aquifer storage sites, one (1) depleted gas field, and one (1) salt cavern field in Europe (Marcogaz, 2017). The latter is in Kiel (Germany) and is now used for natural gas storage.

Most importantly, future hydrogen storage in salt caverns will build on the experience of storing natural gas in salt caverns. It follows similar leaching, debrining and operation steps as illustrated in Figure 2. Due to the size of this natural gas storage industry (nearly 700 salt caverns in about 100 storage sites globally) it is a natural basis for developing storage of hydrogen in salt caverns. New caverns may be closer to these than from the first hydrogen caverns developed in the 70's.



Figure 2: Main developments steps of a hydrogen storage cavern.

1.2. Introduction to Recent Developments

While being based on natural gas cavern designs, hydrogen caverns have some specificities. In the last few years, generally triggered by large scale public funding, technical developments have been made, notably by academic research groups. The purpose of this article is to disseminate recent technical developments made for storage of pure hydrogen in salt caverns and bridge the gap with their application on industrial projects. Several hydrogen-specific topics are presented:

- The tightness of the rock salt to hydrogen,
- The tightness testing of a hydrogen storage cavern (MIT),
- The modelling tools of the thermodynamics of hydrogen stored in a cavern,
- The solubility of hydrogen in residual cavern brine,
- Geochemical interactions with hydrogen (abiotic and biotic reactions), and,
- Well equipment compatibility (steel, elastomers, recommendations per equipment).

2. Tightness to Hydrogen of the Rock Salt

Permeation of fluid into rock salt has been of particular interest for the salt cavern industry. Permeation of brine in salt has proven to be a central phenomenon to consider in the frame of the abandonment of salt caverns (cf. e.g. Brouard Consulting, 2019), and permeation of gas is central to the tightness of the storage. Brückner and Minkley (2016) summarize the knowledge regarding tightness and integrity of salt rocks on the basis of lab tests and in situ investigation. They find that pressure driven percolation takes place only after overcoming a percolation threshold, which is the minimum principal stress. The pressure-driven opening and interconnection of flow paths along grain boundaries is initiated in the salt rock and induces a directional percolation in the direction of the maximum principal stress (the most compressive).

The study of the permeation of hydrogen, rather than brine or other gases, in salt has been more recent. Schlichtenmayer and Bannach, 2015, published the results of measured salt permeability to nitrogen, hydrogen and natural gas at the laboratory and concluded that "*The main result of the permeability measurements is that no significant difference between natural gas, hydrogen and air could be observed. Any difference in the permeation rates of the gases through rock salt results only from their different viscosities. Thus, the results give a positive indication that solution mined salt caverns are in principle as suitable for high pressure hydrogen storage as they are used for natural gas storage for decades*". These tests have been carried out using a transient measuring principle, particularly suited to very low permeability materials. These tests have been done while salt samples are maintained through a confinement pressure (see Figure 3), applying an isotropic stress to mimic the in-situ rock salt stress conditions, which influences the measured permeability.



Figure 3: Experimental set-up described in Schlichtenmayer and Bannach (2015) and some of their results: permeabilities for confinement pressure of 2, 10 and 20 MPa.

However, rock salt at the cavern wall is subject to deviatoric stresses, which generate creep and can damage the rock salt. Permeability measurements under deviatoric stress were recently published in Zhang et al. (2020), summarizing 18 months of experiments. The tests were performed on samples having very low, intermediate (XZ2), and relatively high permeability. The samples used for this testing were from a Cenozoic sedimentary basin in the East of France and were described as composed of large crystal (centimetric size). The permeability of salt samples was evaluated under an isotropic confinement pressure (as Schlichtenmayer and Bannach, 2015, did) as well as under triaxial loading, creating a deviatoric stress in the sample in order to damage the sample during the permeability test. They used a specific triaxial cell equipped with a piston and able to apply an axial stress different to the tangential one that has been used (Figure 4). They observe poromechanical effects: fluid pressure can induce rock skeleton deformation and will have to take place in the stress–strain equation of state characterizing rock salt and the permeability. They also repeated the tests with argon and hydrogen and did not find meaningful differences due to the type of gas.



Figure 4: Left: Experimental set-up described in Zhang et al. (2020) enabling them to measure salt permeability under deviatoric stress conditions, using argon and hydrogen. Right: comparison of the permeabilities obtained using argon or hydrogen as a test fluid for XZ2 salt sample.

Grgic et al. (2022) also investigated the evolution of relative permeability to gas of the rock salt under different loading conditions in the context of hydrogen storage. Under deviatoric loading with low confining pressure (1MPa), they observe an increase permeability due to microcracking, but do not under higher confining pressure (5 MPa). They observe too the self-recovery of damaged salt specimen under creep. They conclude that *"all these results give strong confidence in the underground hydrogen storage in salt caverns which remains by far the safest solution because the different mechanisms (viscoplasticity with strain hardening, microcracking and cracks healing) involved in material deformation act in a competitive way to annihilate any significant permeability evolution".*

Lastly, we may mention AbuAisha and Billiotte (2021) review of the transport mechanisms taking place in the rock salt (intact or damaged):

- Permeation of Hydrogen into the rock salt crystal itself. This phenomenon is responsible for relative permeability to gas of polymer pipes and is happening through steel (and is of interest for salt cavern storage application, since it takes place in elastomer seals or packers and casings, as discussed in section 7). This permeability is important with metals due to the high availability of electrons: at its surface, the dihydrogen molecule can dissociate, and each hydrogen atom ionizes in the H⁺ form, i.e., a proton whose size is much smaller than the distance of the metal crystal lattice. In the case of permeation through halite crystals, the hydrogen atom (106 pm) is larger than the atomic space in the crystal lattice (34 pm) so that the diffusion of hydrogen in the atomic form is not possible. The hydrogen atoms is usually not possible. It follows that the phenomenon of hydrogen permeation in metals and its importance cannot be as significant in rock salt."
- **Diffusion in the interstitial brine**. The porosity of rock salt is initially filled with saturated brine. This porosity, formed by the joints between halite grains, is connected or not. Fickian diffusion of dissolved hydrogen could happen through the connected porosity. This can be modelled however the authors note that *"the experimental determination of the effective diffusion coefficient is challenging"*.
- **Convective flow in the rock salt**, through this connected porosity. Through a single-phase flow (a priori gas), single-phase Darcy law applies. This is what is measured by the above-mentioned Schlichtenmayer and Bannach (2015) or Zhang et al. (2020). At the initiation of a leak, the penetration of gaseous hydrogen into the rock salt implies the displacement of the brine. It is a two-phase immiscible flow in a porous medium, hydrogen being the non-wetting phase and displaced brine the wetting one. Capillary forces should imply an entry pressure. However, field tests using brine and then

(nitrogen) gas did not observe any effect of capillary pressure for rock salt (Durup, 1994), and Brückner and Minkley (2016) mention that it is also the case for numerous laboratory studies.

3. Hydrogen Caverns Mechanical Integrity Tests (MITs)

3.1. Brief Introduction to The Nitrogen/Brine MITs And Their Acceptance Criteria

Since the decisive invention of the nitrogen/brine Mechanical Integrity Tests (MIT) in the 1980's (van Fossan, 1983), salt caverns have the singular advantage that their tightness can be tested very accurately. In its most standard field and interpretation practice today, it implies pressurizing the brine cavern, injecting nitrogen down to just below the last cemented casing shoe and running a log at the start and at the end of the test. Logs enable the measurement of the nitrogen/brine interface depth (and hence deduce the volume of nitrogen in the well) and (in Europe at least) a temperature log (and hence deduce a density log). From the volume and density of nitrogen measured at the start and at the end of the test, a mass balance of the nitrogen can be made, and leaks identified if any. The very small volume, when compared to cavern's one, enables the test to reach extremely good accuracy.



Details on the development of the concern for tightness in the salt cavern industries, of accurate tightness test techniques and of the concept of the MIT can be found in Réveillère, 2021. This work notably shows that the question of the acceptance criteria of MITs came along with the development of the tests. The first attempts were to relate a fail/pass criteria of impacts on groundwater (concept of Maximum Acceptable Leak Rate, MALR). It did not prove practical, as the occurrence of leak paths below ground is practically unpredictable and would be case-specific, which prevents it from setting an industry standard. The alternative approach was to base the test acceptance on the fact that a possible leakage cannot be

distinguished from the accuracy of the test (concept of Minimum Detectable Leak Rate, MDLR) while setting stringent but achievable limits to the MDLR that must be met on the field. It is what is practiced today¹: MIT developers probably still have in mind what is desirable from a groundwater protection point of view, but also the practical impossibility to establish a quantitative MALR. And they can refer to the track record of several decades of salt cavern testing with an accuracy (MDLR) below the reference MDLR values of equivalent 1,000 bbl/y (in North America) or 50 kg/d (in Europe), and to the limited history of leakage incidents from the salt cavern storage industry, especially where recent caverns are concerned. Track records can now weigh more in the balance and be *de facto* accepted as the acceptance criterion, while impact derived MALR are still hardly achievable.

3.2. How Different Should MITs be and Their Interpretation for Future Hydrogen Storage Caverns?

Bérest et al. (2021) propose a tightness test for future hydrogen storage. This work comes as part of the results of a French co-funded collaborative research project (Stopil-H₂) aiming at studying the feasibility of a hydrogen storage pilot, which is now under construction through EU co-funded Hypster collaborative project at Etrez storage site operated by Storengy. It notably suggests using a Maximum Acceptable Leak Rate (MALR) of 50 kg/day. No clear explanation is given, although the fact that hydrogen viscosity is half that of nitrogen and its density 15 times lower are mentioned. From the focus on the MALR, and the use of coefficients to account for fluid properties differences, we can see a parallel with what had been done from the 1980's until Crotogino (1995) included for nitrogen/brine MITs, and may partly be interpreted as Réveillère (2021) did for this period: as an attempt of proposing a rational approach for setting an acceptance criteria (taking the now standard nitrogen / brine MIT as a reference, rather than a possible impact). However, Bérest et al. (2021) are cautious and only use this as an initial proposition: "it can be considered as a provisional initial reference, open to discussion, and to be revised when additional experience (from tightness tests) becomes available".

Bérest et al. (2021) also proposed to run a nitrogen/brine MIT prior to running a hydrogen/brine MIT. Stehouwer (2021) exposed the plans for a pilot hydrogen injection in a salt borehole in Zuidswending site they operate, including a tightness test of successively nitrogen and then hydrogen as a test fluid (this is now done). Interestingly, these two similar propositions of successive MITs with nitrogen and then with hydrogen have been made independently.

Both the concomitant propositions of successive nitrogen and hydrogen MITs in the Zuidswending A8 and Etrez EZ53 pilots, and the lack of a clear rationale argument for proposing an acceptance criterion in Bérest et al. (2021) suggest that a widely accepted tightness test criterion for hydrogen caverns is to be built.

A credible option is that the track record supports that one single nitrogen/brine MIT with conventional acceptance criteria (as detailed above) is relevant for hydrogen as it is for natural gas storage. There is actually no obvious reason why it is not. In the history of MIT development, fluid properties-based analyses have never provided a sound scientific justification to the acceptance criteria, but rather the impression of it, and have not been proven decisive in setting the standards (cf. Réveillère, 2021). Contrarily to the track record of industry-scale as good as practicable testing campaigns and relative absence of incidents. Publication of experiences from the tightness testing and from the integrity record of the six (6) historical hydrogen storage caverns would be important in this view, as the ones from ongoing pilots will be. It will then be possible to propose a standard based on this experience. Until then, we observe that in the two Dutch and French pilots under way, cautious options are taken, such as doubling the tests (nitrogen then repeated with hydrogen).

¹ For instance by Geostock in Europe "the MIT is designed to have an accuracy, or MDLR, lower than a threshold value (50 kg/d of nitrogen), and the well passes if the Calculated Leak Rate is below this MDLR." Réveillère, 2021

4. Thermodynamics of Hydrogen

The thermodynamic properties of hydrogen for the purpose of underground storage have been discussed largely in the literature (Nieland, 2008).

From the thermodynamic point of view, there are two main specificities of hydrogen when compared to natural gas: the Joule-Thomson coefficient and the compressibility factor.

For the underground condition of pressure and temperature, the Joule-Thomson coefficient of hydrogen is negative (in contrary to methane and most gases). It means that, during an isenthalpic throttling, the gas temperature would increase. However, isenthalpic conditions are not met in salt caverns during withdrawal; the impact of this negative coefficient is rather to lead to a smaller temperature variation in the cavern when cycling in hydrogen compared to the same cycles with the natural gas.

The hydrogen compressibility factor is considerably larger than that of methane. This fact results in a smaller working gas compared to the natural gas storage.

A benchmark simulation has been performed using GUSTS V2 (Geostock in-house software) for a hydrogen cavern case presented in Karimi Jafari (2016).

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The cavern parameters are summarized as follows:

- Cavern diameter: 25.6 m (84 ft.)
- Casing shoe depth: 885 m (2,903 ft.)
- Cavern roof depth: 915 m (3,002 ft.)
- Cavern bottom depth: 1,220 m (4,002.6 ft.)
- Cavern volume: 159,000 m3 (1 MMbbl)
- Rock temperature at cavern mid-depth: 38 °C (100°F)
- Maximum pressure: 170 bar (2465 psi), gradient of 0.192 bar/m (0.85 psi/ft.) at casing shoe
- Minimum pressure: 60 bar (870 psi), gradient of 0.068 bar/m (0.3 psi/ft.) at casing shoe

The simulated seasonal gas operation for hydrogen and pure methane constitutes of the following periods:

- 121 days of withdrawal from Pmax to Pmin
- 242 days of injection from Pmin to Pmax

The simulation results, in agreement with Nieland (2008) results, show that for the same operating pressure condition, the hydrogen storage working gas is 20% lower than methane storage working gas for a cavern located between 915 m (3,000 ft.) and 1,220 m (4,000 ft.).

The gas temperature and compressibility variation during a seasonal cycling in the hydrogen and methane cavern are illustrated in Figures 6 and 7 respectively. The working and cushion gas proportion in the hydrogen and methane are presented in Figure 8.



Figure 6: Gas temperature variation in hydrogen and methane cavern (Karimi Jafari, 2016)



Figure 7: Compressibility factor in hydrogen and methane cavern (Karimi Jafari, 2016)



Figure 8: Working and cushion gas volume in hydrogen and methane cavern (Karimi Jafari, 2016)

5. Solubility of the hydrogen

5.1. Availability Data of Solubility in NaCl-Saturated Brines

Solubility of gases in residual brine is not commonly looked at when designing natural gas storage in salt caverns. It is usually assumed to be negligeable, even though no quantitative assessment of it could be found, neither in Perreira (2012) "Common Practices - Gas Cavern Site Characterization, Design, Construction, Maintenance, and Operation" SMRI Research Report nor than, more generally, in the proceedings of the SMRI library².

The question of whether dissolution of hydrogen in residual brine is negligeable or not has however arose in several recent hydrogen storage projects, both commercial and R&D, where Geostock was involved. It is unclear why this question emerged for hydrogen storage while it did not for natural gas storage. We may see the following reasons behind:

- The relative lack of experience in hydrogen caverns when compared to the natural gas storage caverns. Hydrogen storage cavern developers or designers cannot use the fact that dissolved gas in residual brine is not a question for hundreds of other operating caverns.
- The higher cost of hydrogen.
- The fact that significant public fundings are supporting technical developments on hydrogen storage caverns, notably in France through collaborative co-funded projects. These projects involve academic laboratories keen to identify new research topics related to their core research activity.
- Lastly, the fact that while residual brine quantity is minimized for natural gas caverns (highly site specific, a tentative range would be that ~1% to 10% of the cavern free volume remaining in brine), some project developers of hydrogen storage did not want to consider a minimized residual brine volume. They had identified a storage need and an available brine cavern and aimed at debrining just the required volume of the cavern. They usually lack the business model that would enable them to debrine the whole cavern. Typically, they planned to leave 90% of the cavern in brine. The amount of residual brine may therefore be 1 to nearly 2 orders of magnitude higher than for a

² although the search in circa. 2000 papers might not have been detailed enough on all of them

conventional gas cavern. The amount of dissolved gas, at equilibrium, would also be 1 to 2 orders of magnitude higher, possibly making the dissolved gas a significant investment cost, similar to the cushion gas one.

The question of quantifying the amount of residual gas therefore came out for hydrogen and did not for natural gas. Unfortunately, tables of gas solubility in NaCI-saturated brine existed for methane since at least the 60's for instance by Duffy et al. (1960) or Blount and Price (1982) but did not for hydrogen until 2020. Data was also missing for other gases which storage in salt caverns can also bring options in the energy transition: carbon dioxide, oxygen, and nitrogen (together making air). Compressed Air Energy Storage requires air storage. Electrolysis, Methanation and Oxycombustion requires carbon dioxide, oxygen, and methane storage. Using tables of solubilities in pure water would miss the "salting out" effect, which makes gases solubility lower in the presence of salt since water molecules mainly solvate ions and are less available to solubilize gas.

This lack of solubility data has been identified by several research groups in France. They have recently worked on the topic and through the publication of their results, they are bridging these gaps in public knowledge³:

- The Armines CTP (Thermodynamics and Process Center) pursued an experimental approach to develop correlations. They developed solubility tables for O₂ and CO₂ in saturated brine as part of the FluidStory project co-funded by the French Research Agency ANR, leading to Chabab et al., 2021. In similar and related efforts, they pursued the experimental approach and developed correlations for hydrogen within the Rostock-H project also co-funded by the ANR, leading to Chabab et al., 2020.
- The IFPen team developed an approach based on fitting the Sereide and Whitson equation of state calibrated on the data that was then available (Chabab et al. 2020 was not) in Lopez-Lazaro et al., 2019. Roa Pinto et al. (2021) used the e-PPC-SAFT equation of state to fit the available experimental data. This approach is a very detailed model of the physical interactions at play. It was further refined in Kiemde et al. (2022) and extended to O₂ and N₂.
- We may also mention other French research teams currently working on the question, such as the UPPA.

These works have proven to be very complementary. The Armines team has developed experimental solubility tests of hydrogen up to 5 mol/kgw, which had never been done before. From this work, they fit an equation of state that implies a moderate level of physics, they were able to propose tables covering largely salt cavern storage conditions in Temperature (298 - 423 K) and Pressure (5 to 400 bar), but solubility tables *only* for 0, 1, 3 and 5 mol/kgw of pure NaCI. Fully saturated brine corresponds to slightly higher than 6 mol/kgw (e.g., 6.2 mol/kgw at 25°C and atmospheric pressure). They had to limit the salinity due to the risk of clogging of their experimental set-up, they stopped short from testing fully saturated brine.

By modeling details of the physical interactions in the solution through the use of the complex e-PCC-SAFT equation of state, the IFPen team has gained the capacity to extrapolate results further away from the test conditions. In Roa Pinto et al. (2021), they provide model parameters giving solubilities in 6 mol/kgw brines, i.e., for saturated brines.

³ Geostock has not been directly involved in these research works believed to be interesting to our salt cavern community but has accompanied them by being involved along with Armines in Rostock-H and FluidStory research projects, and by financing and co-advising an internship with IFPen

5.2. Application of Recent Research Works to the Estimation of the Quantity of Dissolved Hydrogen in Residual Brine

In the following, we apply some of the results developed by these academic groups and compare them on a salt cavern case. For the sake of simplicity, the case study is the same small cavern as the one exposed in Section 4.

Conditions from Nieland 2008 (& Karimi-Jafari, 2016) Small Cavern Case (Cf. Section 4 for Details)								
	Metric	Metric		Imperial				
Pmin	60	bar	870	psi				
Pmax	170	bar	2465	psi				
Tmin	37	°C	99	F	310,15	к		
Tmax	45	°C	113	F	318,15	к		
Inventory min (CG)	8	M nm3	282	MM scf	719	ton		
Inventory max	21	M nm3	741	MM scf	1,887	ton		
Working gas	13	M nm3	459	MM scf	1,168	ton		

Brine is supposed to be NaCl-saturated. In cavern conditions, taking the average of what is obtained for (Tmin, Pmin) and (Tmax, Pmax) conditions, the salinity is:

Residual Brine Mineralization, at Equilibrium with Halite						
Brine Density	1,192	kg/m ³				
Brine mineralization	318	kg/m ³				
NaCl Mass concentration	27%					
NaCl molality	6.24	mol/kgw				

We consider three quantities of brine left in contact with hydrogen in the cavern:

- <u>The Base Case</u>: Only the minimum reasonable quantity of brine has been left in the cavern. This is the standard practice.
- <u>A Cavern with Very Limited Debrining</u>: For design reason most of the cavern is left in brine during operation.
- <u>Start of a Debrining</u>: The gaseous hydrogen is put in contact with the whole cavern volume in brine. Should dissolution be instantaneous, we could consider that all this brine volume could be saturated in dissolved gas. It is however obviously not the case due to kinetic limitations. This is hard to quantify, but industrial experience from debrinings shows that withdrawn brine is releasing gas only when approaching the end of the debrining. It is however, a technical upper boundary: there is no way more gas could be dissolved.

From the research works presented in the previous section, the solubilities of hydrogen in saturated brine are 0.02% mol fraction in the Pmin, Tmin conditions, and 0.054% mol fraction in the Pmax, Tmax conditions. The results at the cavern scale are presented in the table below.

Debrined Cavern	Limited Debrining	Start of a Debrining	
gas Residual brine	gas Left in brine	gas Not debined yet	
159,000 m ³	15,000 m ³	Not significant	
6,000 m ³	150,000 m ³	165,000 m ³	
1,887,000 kg	178,000 kg	Negligeable	
1,168,000 kg	110,000 kg	N/A	
126 kg 0.007% of the total gas 0.011% of the working gas	3,140 kg 1.8 % of the total gas 2.9 % of the working gas	Dissolved Hydrogen in the brine assuming saturation (highly conservative upper boundary; far from the observations) and at	
350 kg	8,760 kg	= 25°C:	
0.019% of the total gas 0.030% of the working gas	4.9 % of the total gas 7.9 % of the working gas	7,030 kg	
	Debrined Cavern The second se	Debrined CavernLimited DebriningImage: gasImage: gasgasImage: gas159,000 m³15,000 m³159,000 m³150,000 m³6,000 m³150,000 m³1,887,000 kg178,000 kg1,168,000 kg110,000 kg126 kg3,140 kg0.007% of the total gas3,140 kg0.011% of the working gas2.9 % of the total gas350 kg8,760 kg0.019% of the total gas4.9 % of the total gas0.030% of the working gas7.9 % of the working gas	

As a comparison, the cushion gas is 38% of the total gas. This application shows that in the base case (fully debrined cavern), the impact of hydrogen dissolution is absolutely negligeable. In the case of the cavern operating after a very limited debrining, 3% to 5% of the total gas could be dissolved (without a kinetic model of the dissolution and defined cycles, we cannot estimate how it behaves within the cycles). This dissolved hydrogen adds to the cushion gas and increases the quantity and cost of "nonworking gas" by a tenth. This is significant but will probably not lead to stopping a project from considering the solution of a cavern partially debrined if needed.

Lastly, we note that engineering techniques to isolate the brine from the gas were tested in Europe in the 70's to 90's, with mixed to clearly counterproductive results, as summarized in Réveillère et al., 2016. There is no obvious reason for having better results with hydrogen. Without a new technology being proposed, this isolation option is not pursued.

6. Geochemical Interactions with Hydrogen

As hydrogen is an electron donor, it is a very attractive source of energy for numerous reactions under biotic or abiotic environment, (with or without active microorganisms). This potential reactivity under salt cavern environment will be reviewed in the following chapters.

6.1. Abiotic Reactivity of Rocks with Hydrogen

Although hydrogen storage in salt caverns has existed in several sites since the 70's, there is no published case study where it is possible to observe in-situ geochemical reactions during storage operations.

In the public information on the 6 existing hydrogen caverns operating for sometimes more than 50 years, there is no mention of loss of the stored hydrogen by geochemical reactions or microbiological activity. There is in general limited public information on the quality of the withdrawn gas, besides the following two from Air Liquide, the operator of the Spindeltop cavern that started operating in 2014. Jallais (2021) mentions "No pollution & contamination of the gas" among advantages of salt cavern storage of hydrogen. The same author considers a "Purification unit" in the surface equipment of an H₂ storage site in salt cavern but associates a "negligeable" cost to it in Ineris, 2021. Through a personal communication with an operator of a H₂ storage cavern, the feedback was that they detected H₂S in the withdrawn gas at the begining, and that it went away without any action on their end. The fact that another hydrogen cavern has detected H₂S was also mentioned. From these feedbacks on the existing hydrogen storage caverns, we note that the impact of the microbiological activity is not a question of product loss, possibly a question of product quality and corrosion, and that it is probably much more common than in hydrocarbon storage caverns.

Concerning pure abiotic reactivity, several geochemical models were developed to attempt to predict the reactions between the minerals and hydrogen, most of them in the context of storage in depleted gas fields or aquifers, which is known to be more reactive than salt caverns in the presence of hydrogen. Nevertheless, it is possible to find some models that were simulated in the salt cavern environment as the one developed by Hemme and van Berk (2017), but it takes into account bacteria activity, therefore it will be treated in next chapter.

Within the ROSTOCK-H project, geochemical reactions experiments were performed without any bacteria presence (Ineris, 2021). Transport was not taken into account in this model. Salt rocks were composed mostly of halite, but also anhydrite, dolomite, pyrite, quartz, barite and siderite.

Results from experiments were reassuring as halite, which is the main component of salt rock, was not dissolved with a large amount of hydrogen.

Nevertheless, elements contained in insoluble phases could react in contact with hydrogen. Especially:

- Elements containing sulfate (barite and anhydrite) could be dissolved and transformed into sulfide elements due to the reduction effect of hydrogen.
- Elements containing carbonates (dolomite and siderite) could be dissolved and transformed into methane due to the reduction effect of hydrogen.
- Iron should remain as pyrite or mackinawite. But as sulfide content could increase, pyrite or pyrrhotite fraction could increase.

These reactions should come with pH increase based on the following reactions that release hydroxide ions (Jacquemet N., 2020).

$$SO_4^{2-} + 4H_2 \Leftrightarrow H_2S + 2H_2O + 2HO^-$$

$$HCO_3^- + 4H_2 \Leftrightarrow CH_4 + HO^- + 2H_2O$$

Nevertheless, the kinetic of these reactions seems to be very slow without an external catalyser as bacteria or high temperature (>200°C) (Ineris, 2021). This point was highlighted in HyStorPor UK-funded project in which more than 300 laboratory geochemical tests were conducted at high pressure (between 0.1 and 200 bar) and temperature between 50 and 80°C⁴. They carried out tests with pure minerals as calcite, dolomite, gypsum and pyrite, and various cores from reservoirs. These elements were put in contact with hydrogen.

⁴ Webinar HystorPor (2022) <u>https://blogs.ed.ac.uk/hystorpor/category/news/</u>According to the presenter, an article will be published soon.

So far, they concluded that there was no risk of hydrogen loss due to geochemical reactions during geological storage.

First tests performed in the EU-funded Hystories⁵ project drew the same conclusions. If reactions and consumption of hydrogen are observed in biotic environment (see Section 6.2), so far there is no hydrogen consumption that is observed in abiotic environment (publication on-going).

Therefore, in a salt cavern below 200°C and in the absence of bacteria, the risk of geochemical reactions between minerals and hydrogen is considered very low. Reactions are thermodynamically possible, although their kinetics under storage temperatures prevents them from happening in abiotic conditions. But a wide range of bacteria can catalyse these thermodynamically possible reactions to convert part of this potential energy to cellular energy.

6.2. Microbiological Activity and Impacts

In the presence of microorganisms, the likelihood of geochemical reactions and the kinetics can increase.

The fact that underground storage can host bacteria has been broadly documented even in salt caverns. Fournier et al., 2020. Nevertheless, their diversity and their concentration are known to be decreasing, when salinity increases.

To illustrate this point, the three major oxidizing groups of bacteria are represented in the graphs below. Their optimal and critical growth are indicated in function of temperature, pH and salinity.

⁵ www.hystories.eu



Figure 9: Distribution of optimum growth temperature, pH and salinity for methanogens, homoacetogens and sulphur species reducing microorganisms (Thaysen & al, 2021)

It is observed that bacteria development becomes difficult when the temperature is above 100°C, pH above 10 and salinity above 3.9 mol/kgw (228 g/L of NaCl).

Therefore, if bacteria growth is possible in a salt cavern, when brine in saturated in NaCl (~330 g/l in cavern conditions), their observation is quite rare. Furthermore, their kinetics will be slower than in a less saline environment (Ineris, 2021). Lastly, bacteria tends to develop in contact with solids and to form biofilms. In salt caverns, in comparison to porous media, the specific surface of solids is very poor, bacteria will have less surface to develop their interactions between water and minerals, which will also tend to decrease the reactions rate as observed at the cavern scale.

It should be reminded that to be active, bacteria need to be in contact with water, in which they will find most of their nutrients to grow. Main nutrients used are carbon, nitrogen, and phosphor. Bacteria can remain for several years in a dormant state when they do not find nutrients anymore (Ineris, 2021).

In the presence of hydrogen, some bacteria will react with its electron donor properties. Main reactions are summarized in the schematic below.



Figure 10: Main reactions mechanisms in presence of hydrogen (schema from MicroPro)

Main microorganisms able to react in presence of hydrogen are:

- Sulphate reducing bacteria and archae
- Methanogenic archae
- Ferric reducing bacteria
- Acetogenic bacteria

The two last types of bacteria have less impact on gas quality, therefore, most of the studies are focused on the two first types of bacteria.

These reactions were highlighted in laboratory experiments. For example, laboratory studies from Nitschke-Kowsky (Nitschke-Kowsky, 2012) did not observe any change in gas composition or biofilm production in experiments containing 8 % hydrogen in natural gas, unless carbon dioxide and nutrients were added.

MicroPro in partnership with Geostock highlighted the same phenomenon of hydrogen consumption when a mixing of hydrogen and CO_2 was in contact with sulphate reducing bacteria immersed in saturated brine (300 g/l of NaCl) with various nutrients.



Figure 11: Gas volume variation due to sulphate reducing bacteria reaction (internal document from Geostock and MicroPro)

On this graph, it is visible that consumption of hydrogen was the highest with paraffin or trimethylamine. These nutrients may not be present in the underground salt cavern at the beginning of hydrogen storage, nevertheless, some bacteria could produce acetate for example, which will then be used as nutrients to consume hydrogen.

In RINGS project⁶, 10% of hydrogen was introduced in a closed reactor containing formation water with its microorganisms, rock samples from porous media (mainly composed of quartz, calcite and barite), and natural gas. After the introduction of hydrogen, different reactions occurred successively. First, a development of sulfate reducing bacteria was observed. These bacteria consumed the sulfate ions in water and dissolved barite minerals. When all the sulfate ions were consumed, a second phase started with the development of methanogenic bacteria. These bacteria consume carbonate and tend to dissolve carbonate. In the gas phase, hydrogen and carbon dioxide were progressively consumed and methane appeared.

On the last example, it is specified that water was less saline than brine from salt cavern. Based on Ineris, 2021, methanogenic activity from bacteria were observed until 100 g/l in NaCl, whereas acetogenic or sulfate reducing bacteria were observed at higher salinity. Therefore, it is supposed that the main bacteria reaction in a salt cavern would be the consumption of hydrogen and the formation of hydrogen sulfide with the help of sulfate reducing bacteria.

This reaction was especially studied in Laban modelling. It was highlighted that the loss of hydrogen by bacterial conversion to H_2S via sulfate reduction is limited mainly by the amount of sulfate available in the salt rocks.

The sulphate used for these bacteria catalyzed reactions are available due to anhydrite (CaSO₄) dissolution, available in the sump and cavern wall (Laban M. P., 2020). The following schema summarizes the reaction that would happen in a storage catalyzed by bacteria:

⁶ As presented by Paula Haddad during her PhD thesis defense. The thesis itself is not publicly available yet.



Figure 12: Simplification of the main reactions considered for the production of H2S (Laban, 2020)

The kinetic rate of the reaction between sulphate, hydrogen and bacteria can be modelled through a multi-Monod equation (Laban M. P., 2020):

$$Rate \; = k \; imes kgw \; imes \; rac{SO_4^{2-}}{0.\; 001 + \; SO_4^{2-}} \; imes \; rac{H_2}{0.\; 001 + \; H_2}$$

Where k is the kinematic rate and kgw is the mass of available brine. In Laban thesis, a kinetic rate of 9.10-10 mol.kgw-1.s-1 was assumed.

With this equation, Laban estimated that after 10 years, a first case leads to 0.04 ppm of H_2S production, and the other up to 24 ppm, or 0.0024 %. This apparition of H_2S may require treatment, but it is not a significant hydrogen loss.

In the model from Hemm and van Berk, rock salts contain anhydrite (CaSO₄), which is a potential source for H_2S generation (Hemme & van Berk, 2017). It indicates that reactions were highly dependent on bacteria activity and sulphate concentration in the water phase.

Other modelling suggests that the H₂S production rate evolves initially from the rate of aqueous redox interactions between sulphate and the dissolved gas in the underground storage to the rate of diffusion-controlled dissolution of anhydrite (Bildstein, Worden, & Brosse, 2001). Therefore, the H₂S production rate should become slower once all the dissolved sulphate in brine would have been consumed.

Furthermore, as it is expected to observe pH increase with the reaction between sulfate and hydrogen, the H_2S percentage in gas phase should be even lower. In the case of H_2S apparition in gas phase, several solutions can be applied to treat it in situ. For example, FeCl₂ or NaOH can be introduced inside the cavern. With the former, sulphide will react with ferrous ions to form mackinawite precipitates. With the latter, pH of the brine will increase, which should slow down bacterial growth, and the type of sulphide species will shift from H_2S to HS^- or even S^{2-} .

Lastly, the first priority is to limit any bacteria development in salt cavern during the whole life of the storage. To do so, it is recommended to use water that is bacteria-free during the leaching of the cavern. Then, during operation, regular water quality monitoring shall be set up. In case of bacteria development and especially sulfate or thiosulfate reducing bacteria, biocide treatment should be considered.

7. Well Equipment Compatibility

If standards exist for surface facilities in contact with hydrogen (ASME B31-12), there is no such document for sub-surface equipment. Moreover, environment in sub-surface is different due to water saturated atmosphere and traces of other gas components (as CH₄, H₂S, O₂, CO₂, etc.). In this chapter, state of the art of steel and elastomers compatibility will be presented. Lastly, recommendations for well equipment for hydrogen service will be proposed.

7.1. Steel Compatibility

Once adsorbed on metallic surface, dihydrogen can be dissociated into its atomic form. Then, the hydrogen atom is so small that it can penetrate the metal. Defects within the material, which create interstitial sites, result in hydrogen trapping, which decreases transport kinetics and increases the local hydrogen concentration. The trapped hydrogen will then tend to accumulate, causing loss of ductility and decrease in toughness. Moreover, if two atoms meet in a defect in structure, they recombine to a molecule. The molecule is immobile in the lattice. The accumulation of hydrogen molecules in a defect leads to a decrease of load capacity before cracking. This phenomenon is known as hydrogen embrittlement.

According to the (Netherlands Enterprise Agency (NEA), 2017), standard casing and tubing metallurgy can be used to store/transport gas with hydrogen concentration lower than 0.5%. For hydrogen concentration, lower than 10% the studies performed on material so far have shown no critical impact for wet gas. Whereas when hydrogen is above 10%, the NEA does not recommend any specific material but stipulates that all the well completion components that are in direct contact with hydrogen (example inner casing, cement, subsurface safety valve, packer, etc.) must be hydrogen resistant.

It has been shown that carbon steel could be hydrogen resistant provided that the following conditions are met:

- The tensile strength must be less than 800 MPa to be compatible with hydrogen according to the EIGA IGC standard (EIGA 121/14, 2014) or even lower than 550 MPa according to ASME_STP-PT-006 (ASME_STP-PT-006, 2007).
- Its chemical composition shall be monitored with attention. Especially, phosphor and sulphur contents shall be lower than 0.015% and 0.01% respectively. Furthermore, the manganese / carbon ratio should not be too high in order to limit hardening and weldability problems. It is recommended to maintain a Carbon Equivalent (C + Mn / 6) below 0.43 (EIGA 121/14, 2014).
- A maximum hardness of 22 Rockwell C (250 HV) is specified. This parameter shall be especially respected in welding areas and heat affected zones, where this parameter is often harder and therefore more susceptible to embrittlement than the base metal. Post Weld Heat Treatment (PWHT) is recommended to decrease hardness of the weld areas.
- Surface state of the steel shall be defect free. As a matter of fact, notches or pitting can increase hydrogen embrittlement risks.
- Lastly, additional safety factors shall be added to remain conservative concerning the constraints applied on steel equipment in the presence of hydrogen.

Austenitic stainless steels (316 / 316 L) are also a good option for hydrogen service. As per ASME_STP-PT-006, they appear to be the best choice for hydrogen piping systems with regard to resisting hydrogen embrittlement. On the contrary, martensitic, ferritic and duplex stainless steels are not recommended.

These assessments found in surface facilities standards are valid for pure and dry hydrogen. When withdrawing from a salt cavern, it is considered that hydrogen will be wet. It is also considered that other traces of gas components could be present as CH₄, O₂, CO₂ or H₂S, even if these pollutants are less likely to appear in salt cavern than in porous media.

Impacts of these pollutants will be different depending on their nature.

Methane is considered neutral in regards to hydrogen embrittlement.

Dissolved oxygen on the contrary will have an impact on steel. On carbon steel, it will passivate the surface with an oxide layer and therefore the permeation of hydrogen will be slowed down (Briottet, 2018). 316 L

stainless steel was found to be susceptible to localized attack (pitting) in partially deoxygenated water (Mark & Carminati, 2008). This pitting could increase hydrogen embrittlement. Therefore, depending on oxygen concentration in gas phase and water phase, carbon steel could be preferred to 316L.

Concerning H_2S , it was observed that its presence will increase hydrogen permeation into the metal (CEFRACOR, 2016). Nevertheless, its impact in the term of cracking in saline and wet environment was not studied broadly. As part of the Hystories project, tests on steel were conducted in autoclave in presence of electrolyte, hydrogen and traces of CO₂ or/and H₂S. These tests confirmed that in the presence of H₂S, hydrogen content inside carbon steel material (L80 or K55) was higher (see graph below).



Figure 13: Hydrogen uptake of steel K55 in autoclave tests at room temperature with 120 bar of H2 left side and 120 bar of H2 + 1 bar of H2S right side (Loder, 2022)

Nevertheless, the steels submitted at 90% of its SMYS (Constant Load Test) did not crack after 720 h in any conditions. Therefore, L80 or K55 could be compatible with hydrogen application, with or without humidity, with or without CO_2 (up to 0.11% mol), with or without H₂S (up to 0.008% mol) (Loder, 2022). Tests on 316L are still on-going.

7.2. Elastomers Compatibility

Currently, there is no specific standard for well equipment such as packers and bridge plugs for hydrogenrich gas. The current standards such as API SPEC 11D1 or ISO 14310:2008 test them for gas with air, nitrogen or other gas or mixture of gases.

In the wells, elastomeric seals are used in the majority of completion elements: packers, wellhead, safety valves. The polymers and elastomers are mainly investigated in the case hydrogen under high pressure for commercial application prospects such as, the development and use of the fuel cell vehicle and hydrogen fuel station. The study of the resistance of elastomer seals to pressure under a hydrogen atmosphere has been little studied.

Depending on the nature of the material, elastomer may be strongly impacted by hydrogen contact which may be quantified as shown in figure below :



Figure 14: Specific volume changes for thermoplastics (POM, Nylon, EPOM, PTFE) and elastomers (Viton A, Buna) after exposure to Ar/H2 (Menon & al, 2016)

Note that other types of elastomers are chemically compatible with hydrogen but are not compatible with methane. This is the case, for example, of EPDM (Ethylene-Propylene-Diene Rubber).

Common rubber polymers used in oilfield equipment seals are fluorocarbon (FKM), nitrile (NBR), hydrogenated nitrile (HNBR). These materials are typically used to manufacture seals for a mechanically set packer. These rubber polymers are used both in thin cross-section seals such as O-rings, as well as thicker cross-section seals in packer elements. Due to having a higher modulus than swellable-type rubbers, NBR, HNBR and FKM materials are more resistant to Rapid Gas Decompression (RGD) damage than compounds designed to swell in oil or water (Young & al, 2011).

The study on Ethylene Propylene-Diene Monomer (EPDM) and nitrile-butadiene rubber (NBR) having carbon black (CB), silica (SC), and no fillers (NF) shows that the hydrogen content in the rubber follows Henry's law, which means that hydrogen penetrates into the rubber materials (Young & al, 2011).

As seen above, hydrogen permeation into elastomers can greatly fragilize and eventually jeopardize any elastomer seals. Consequently, all elastomer seals to be used downhole, such as production packer seals and wellheads P-seals, should be certified for hydrogen. Several standards are already available to qualify elastomers mainly for hydrogen transport (EIGA 121/14, 2014). Marcogaz recently recommended examining the parts of the existing operational subsurface equipment before injection of hydrogen for the envisaged storage operating conditions (Marcogaz, 2017). The influence of other gas components (CO₂, H₂O, O₂) must be taken into account. However, no special issues were published for former town gas storages. There are sealing elements which are resistant to hydrogen and already used in the hydrogen industry.

7.3. Review of the Recommendations for Well Equipment

The list below summarizes the downhole equipment that would be in contact with hydrogen:

- Wellhead and its valves and tightness joints
- X-over
- Downhole safety valve
- Production packer
- Landing nipples
- Casing below packer
- Tubing

For seamless tubing and casing, their connections could be welded and threaded but shall be certified for hydrogen application. Two alternatives are possible depending on gas purity, depth of the well and budget: Carbon steel or austenitic stainless steel (316L). If carbon steel is selected, the conditions mentioned in the steel compatibility paragraph shall be respected. It would be preferred to select carbon steel with low yield strength (L80 or lower).

Austenitic stainless steels or new alloys developed for hydrogen application would be recommended for steel elements that undergo significant constraints as accessories elements inside the completion (safety valve, landing nipple).

Concerning packer, it is recommended to decrease the thickness of elastomers which will reduce hydrogen trapping inside the elastomers and thus the risk of cracking in case of rapid decompression. It will be necessary to check that this elastomer is compatible with hydrogen application.

For seals in the wellhead, a metal seal would be preferred to elastomers to decrease permeation risks. Most of the current wellheads are in low alloy AISI 4130. So far, there is no contraindication towards the use of this material in hydrogen service. Nevertheless, carbon steel cladded with 316 L could also be a good option.

No matter what, the role of suppliers will be essential to develop and certify all key well completion equipment for hydrogen application in underground storage.

8. Conclusion

There is nearly 50 years' industrial experience of hydrogen storage in salt caverns, which is essentially similar to natural gas storage in salt caverns for which there is extensive experience.

However, numerous developments have been brought over the past few years, largely triggered by public co-funding to collaborative research projects now that many countries have ambitious development plans for hydrogen storage in salt caverns, as part of the energy transition.

The present work aimed at presenting and summarizing some of these recent technical developments in order to disseminate them.

Hydrogen storage sometimes raises specific questions when compared to natural gas. Hydrogen is a strong electron donor and is a very attractive source of energy for numerous reactions under biotic or abiotic environment (with or without active microorganisms). Reactions are thermodynamically possible, although their kinetics under storage temperatures prevents them from happening in abiotic conditions. But a wide range of bacteria can catalyse these thermodynamically possible reactions to convert part of this potential energy to cellular energy, even in very saline conditions. Although, laboratory tests and the few modelling exercises suggest that at cavern scale, that may be a purity question on some caverns but should not have significant effect on hydrogen loss. This is supported by the scare feedback available from the 6 caverns in operation. Additional feedback from operating hydrogen caverns would be highly desirable. Plus, in case it would happen, in-situ treatments can be considered. Similarly, hydrogen raises steel embrittlement questions that do not exist for natural gas and increased permeation in elastomers, raising new questions

when designing salt cavern wells. This is investigated by several research project at lab scale, most notably through the Hystories project in MU Leoben laboratories, and will enable to support recommendations for future designs. For well equipment (wellheads, packers and downhole safety valves), in the absence of applicable API standard, the role of suppliers will be essential to develop and certify all key well completion equipment for hydrogen service in underground storage.

In some other cases, the industry is trying to adapt its standards or tools from natural gas to hydrogen storage. It is for instance the case when proposing tightness testing procedures (MITs) for hydrogen storage in the current hydrogen storage pilots in France and the Netherlands (resp. Stopil-H2/Hypster led by Storengy and Pilotproject A8 led by Gasunie), both taking relatively conservative approaches by successively testing with nitrogen and then with hydrogen. Standard natural gas caverns are not successively tested with nitrogen and then natural gas, but with nitrogen only, which has been proven effective as a final validation test of the cavern integrity. Internal developments have also been brought, such as Geostock enabling its internal thermodynamic simulation software to cope for hydrogen when developing GUSTv2.

Last, there are developments that are made for hydrogen storage caverns but not for natural gas, partly due to the high interest of academic research groups led to hydrogen by public funding agencies. We may find such influence in the recent interest in the solubility of hydrogen in residual brine, even if not looked at for natural gas caverns. Although in that case Armines and IFPen research teams also bridged a knowledge gap for hydrogen that did not exist for methane. This influence is clearer for salt permeability test under deviatoric stress conditions as developed by Ecole Centrale Lille. In these cases, the developments made for hydrogen storage will be applicable and profitable more generally to the salt cavern community.

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