Development of an Integrated work-flow for Biochemical Underground Hydrogen Storage Modelling

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Abstract

With energy transition happening in the next future years, a significant amount of variable renewable energy production from wind and solar power plants will be added to the national energy system. This condition will determine the need for large amount and long term storage facilities that can handle the seasonality of renewable electricity generation. The transformation of such electricity into chemical energy generating hydrogen using electrolysers is getting more and more attention. Once the H_2 molecules are produced they have to be stored for long periods of time and since up-surface tanks are not suitable to completely fulfil the task, research is focusing on Underground Hydrogen Storage (UHS) as an alternative. This type of storage can be done in four different sub-surface formations: lined rock caverns, salt caverns, deep aquifers, and depleted oil and gas fields.

Many aspects of UHS require dedicated studies to be completely understood. During an internship with ENI in the ARMS (Advanced Reservoir Modelling and Simulation) department this thesis was developed to get a deeper knowledge on two different aspects that are relevant to implement H_2 storage in a realistic depleted gas field facility:

1. The main bio-chemical activity that takes place in underground formations i.e. Methanogenic Archaea proliferation is studied, modelled and simulated. Its impact depending on reservoir conditions and operational choices is evaluated through a sensitivity analysis considering various parameters.
2. The main storage operability parameters are varied in order to develop a systematic approach to assess: realistic storage capacity, cushion gas type and amount. Furthermore, a sensitivity analysis on scheduled charge/discharge flowrates is done to better understand the real potential of this technology in future projections of a completely decarbonized national energy system.

To complete the first task, an ad-hoc work-flow to model the proliferation of Methanogenic Archaea based on H_2 and CO_2 aqueous concentration in the sub-surface field was implemented using a commercial reservoir simulator. Together with it, the Vapour-Liquid equilibrium constant at reservoir conditions for each component in the fluid mixture were added. The above methodology was then applied in a representative sector model of a real depleted gas reservoir (the Nissa field), modifying numerous input parameters. Results showed that a large amount of CO_2 in reservoir is actually an issue, but if this parameter is kept under control the maximum H_2 loss due to methanogens remains below 3% with respect to the same case without microorganism.

Regarding the second task many configurations have been simulated to evaluate the actual potential of the Nissa field without including the microorganism losses that, as highlighted in the first part of the work, would have had a marginal impact on hydrogen losses.

The impact of the cushion gas molecule and amount was studied together with the number of wells to use, the aquifer influx importance and the benefits deriving from a flexible schedule. Results showed that:

- H_2 molecule as a cushion gas is from a technical point of view preferable even if CH_4 option might be cheaper.
- Critical aspects like the possibility to insert an idle period between the cushion gas injection and the 1st injection of operation might increase the estimated capacity of the specific facility
- Flexible switching between injection and production operation on daily basis brings benefits on water management and gas production stream purity

Key-words: Hydrogen; underground hydrogen storage; microbial hydrogen consumption; methanogens; hydrogen storage plant operation

Abstract in italiano

Con la transizione energetica in atto nei prossimi anni, al sistema energetico nazionale si aggiungerà una quantità significativa di produzione variabile di energia rinnovabile da impianti eolici e solari. Questa condizione farà sorgere la necessità di impianti di stoccaggio di grandi dimensioni e di lunga durata, in grado di gestire la stagionalità della produzione di energia elettrica rinnovabile. La trasformazione di tale energia elettrica in energia chimica legata all'idrogeno mediante elettrolizzatori sta ricevendo sempre più riconoscimento in ambito scientifico. Una volta prodotte, le molecole di H_2 devono essere immagazzinate per lunghi periodi di tempo; poiché i serbatoi in superficie non sembrano essere in grado di svolgere completamente questo compito, molti studi si stanno concentrando sullo stoccaggio sotterraneo dell'idrogeno come alternativa. Questo tipo di stoccaggio può essere effettuato in quattro diverse formazioni sotterranee: caverne di roccia rivestite artificialmente, caverne saline, falde acquifere profonde e giacimenti di petrolio e/o gas esauriti.

Molti aspetti di questo tipo di stoccaggio richiedono progetti dedicati per essere completamente compresi; questa tesi, svolta durante un tirocinio presso Eni nel dipartimento ARMS (Advanced Reservoir Modelling and Simulation), si concentra principalmente su due diversi aspetti che sono rilevanti quando si studia un caso realistico di un campo a gas esaurito:

1. La più impattante attività biochimica che ha luogo nelle formazioni sotterranee, ossia la proliferazione di agenti metanogeni, viene studiata, modellata e simulata. Il suo impatto, che dipende dalle condizioni del giacimento e dalle scelte operative, è stato valutato attraverso un approccio di analisi di sensitività su diversi parametri.
2. Le principali variabili di operatività dell'impianto vengono modificate al fine di sviluppare una procedura universale per comprendere: la capacità di stoccaggio reale, le strategie decisionali riguardo il cushion gas. Inoltre, è stata aggiunta un'analisi finale sulla flessibilità della portata programmata, per comprendere meglio il reale potenziale della tecnologia di stoccaggio nelle proiezioni future di un sistema energetico nazionale completamente decarbonizzato.

Per realizzare il primo task è stata eseguita una procedura di messa a punto per modellare il tasso di proliferazione degli agenti metanogeni in base alla concentrazione acquosa di H_2 e CO_2 nel campo. Insieme ad essa, è stata effettuata la stima della costante di equilibrio liquido-vapore alle condizioni del giacimento per ciascun componente della miscela fluida. Una volta affrontate completamente le questioni tecniche, sono state effettuate analisi di sensitività che hanno mostrato che una grande quantità di CO_2 nel serbatoio è effettivamente un problema, ma se questo parametro viene tenuto sotto controllo la perdita massima di H_2 dovuta ai metanogeni rimane inferiore al 3% rispetto allo stesso caso senza microrganismi.

Per quanto riguarda il secondo task, sono state simulate molte configurazioni per valutare l'effettivo potenziale del campo Nissa senza includere le perdite di microrganismi che avrebbero avuto un impatto marginale in uno scenario di lungo periodo come dimostrato dall'analisi precedente.

Da questo punto di partenza è stato possibile valutare l'impatto della molecola e della quantità di cushion gas, il numero di pozzi da realizzare, l'importanza della spinta dell'acquifero e i benefici correlati a una programmazione flessibile delle portate da iniettare e produrre. I risultati finali mostrano che:

- La molecola H_2 come cushion gas è preferibile da un punto di vista tecnico anche se l'opzione CH_4 potrebbe essere più economica,
- Aspetti critici come la possibilità di inserire un periodo di inattività tra l'iniezione del cushion gas e la prima iniezione di esercizio potrebbero aumentare la capacità stimata dell'impianto specifico
- Il passaggio rapido tra un periodo di iniezione e uno di produzione può portare forti benefici alla gestione dell'acquifero e alla purezza del gas prodotto.

Parole chiave: Idrogeno; stoccaggio sotterraneo di idrogeno; consumo microbico di idrogeno; metanogeni; impianto di stoccaggio sotterraneo di idrogeno

Contents

Abstract ii

Abstract in italiano iv

Contents vii

Introduction 1

1 Hydrogen for energy transition 5

1.1. Can Hydrogen substitute Natural Gas? 5

1.2. Underground hydrogen storage 8

1.2.1. Lined hard rock caverns 10

1.2.2. Salt caverns 10

1.2.3. Depleted gas reservoirs 12

1.2.4. Aquifers 13

2 Literature Review on related projects 14

2.1. Hystories 15

2.2. HyUnder 16

2.3. HyUSPRe 16

2.4. HyStock 16

2.5. HyPSTER 17

2.6. H2STORE and HyINTEGER 17

2.7. Hychico and Underground Sun Storage 17

3 Depleted gas field description and biological activity modelling 18

3.1. Field Overview 18

3.2. Biological activity 20

3.2.1. Microbial reactions analysis 20

3.2.2. Microbial growth Chemical & Mathematical description 21

3.2.3. Microbial transport & Physical properties influence 23

3.3. Modelling Tools 24

3.3.1. STARS simulator 25

3.3.2. ECHELON simulator 26

4 Effects of methanogens archaea on UHS 27

4.1. General introduction 27

4.2. Base Case definition & Analysis 30
4.3. Methane as Cushion Gas 33
4.4. Carbon Dioxide as Cushion Gas 35
4.5. Different Initial Carbon Dioxide amount in reservoir 37

5 Realistic Energy Scenarios and Applications for UHS 38

5.1. General Introduction 38
5.2. Base Case Definition & Analysis 40
5.3. Methane as Cushion Gas 44
5.4. Different amount of Cushion Gas injected 46
5.4.1. Reduced Cushion Gas injected 46
5.4.2. Increased Cushion Gas injected 48
5.5. Different Number of Wells in operation 50
5.5.1. Seven operating wells case 50
5.5.2. Ten operating wells case 52
5.6. Realistic storage operation scenarios 53
5.6.1. Monthly flexible Schedule 55
5.6.2. Daily flexible Schedule 57

6 Conclusion and future developments 61

6.1. Underground Chemistry 61
6.2. Reservoir Storage Operability 62

Bibliography 64

A Appendix A 67

List of Figure 70

List of Tables 72

List of symbols 73

List of Acronyms 75

Acknowledgments 77

Introduction

Hydrogen [H] is the most present element on earth. In its molecular form H_2, hydrogen can be seen as an energy source able to provide a high energy per unit mass LHV = 120 MJ/kg if compared to other similar gaseous fuels like Natural Gas (NG), around 49 MJ/kg depending on the specific composition, and even more with respect to liquid fuels, around 42-44 MJ/kg, that are commonly used in the transport sector. Anyway, in order to suggest a fair comparison, the extremely low density of H_2 with respect to NG and even more with respect to liquid fuels, made its utilization as a fuel not very attractive in the past years, since bigger volumes are required in order to store the same amount of energy. This statement about H_2 remains true and have to be considered in every application: it may be tackled by increasing the storage pressure while bringing down the temperature in order to stimulate the molecule transition from the gaseous to the liquid phase in surface-tank storages.

Furthermore, the energy released by a fuel is in the form of heat, so in order to be usable for a final consumer, in a multi-sector energy modelling scenario, a thermodynamic system has to be considered to transform heat into mechanical energy and if necessary, an electric generator is used to finally get electrical energy. This leaves the use of H_2 as a fuel mainly to the hard to abate sectors that cannot be easily electrified such as steel manufacturing, heavy-duty road transport, shipping and aviation. [1] A more recent way to consider H_2 is as a reactant together with O_2 in RedOx reactions typical of fuel cells . In this way chemical energy is directly transformed into electricity and a much higher overall efficiency in the process is reached.

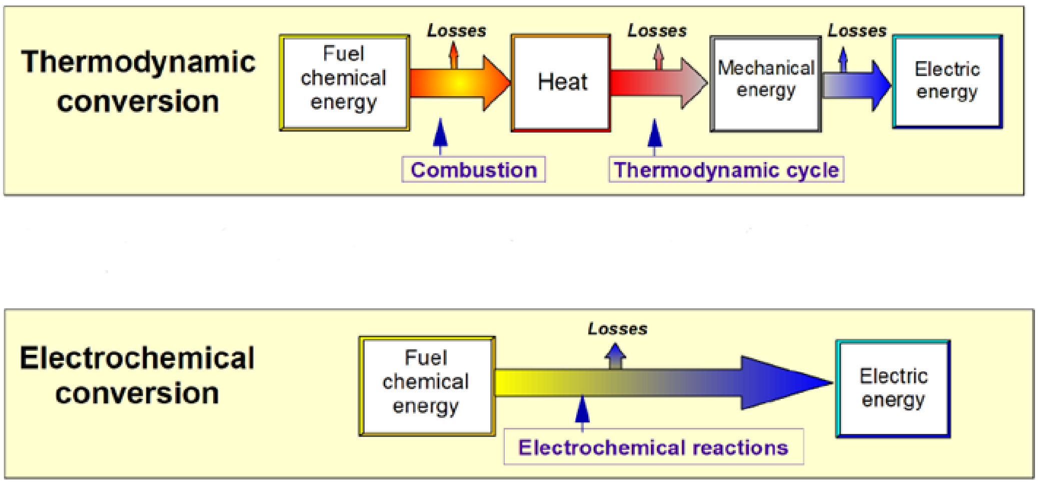


Figure 0-1: Thermodynamic vs Electrochemical Conversion to final Electric Energy

Unfortunately though the H_2 molecule can't be found directly in Nature, for the most part Hydrogen bounded with oxygen (H_2O Water) or carbon (CH_4 methane) in the atmosphere and underground. So, hydrogen is better to be considered as an energy vector rather than an energy source since energy is required to get H_2 from a more complex molecule like CH_4 or H_2O with the respective processes named: Steam Reforming and Electrolysis.

Historically, during the development of modern industry hydrogen played a role in a very wide range of applications:

- Synthesis of NH_3 (Ammonia), a chemical intermediate useful to produce fertilizers in agriculture,
- Synthesis of CH_3OH (Methanol), a molecule that can be obtained utilising CO_2 and that recently has seen an increasing interest in order to meet the Net-Zero CO_2 emissions target,
- H_2 itself inside Refineries, in order to produce final liquid fuels from crude oil.

So it's not very surprising that already in the early 20th century the idea of using hydrogen as an energy carrier for a system of renewable energy production was discussed by the Briton J.B.S. Haldone in a speech at the Cambridge University. Later on, J.O. Bockris first used the term "hydrogen economy" in 1972 to describe a system in which energy is stored and distributed as hydrogen gas [2].

Nowadays, the need to reduce GHG emissions has re-aroused the interest in hydrogen potential as a zero-carbon energy vector in order to facilitate the penetration of renewable energy generation. This type of energy comes primarily from Sun and Wind and it is characterized by non-predictability, intermittency and seasonality due to weather changing with different time scales (days, weeks and seasons). In a strongly time dependent renewable energy production scenario, hydrogen generation and the storage is going to play a key role in order to smooth the over/under production periods and meet the final electricity demand.

Considering the different time scales in play, hydrogen alone cannot be the solution to the storing problem but for sure can be part of it thanks to its high energy density. The reason why H_2 has this advantage over other storing technologies like Pumped-Hydro Storage (PHS) and Compressed Air Energy Storage (CAES) relies in the way in which electrical energy is stored: in PHS it becomes potential energy, in CAES becomes compression energy while in H_2 generation through electrolysis, it becomes chemical energy. Battery storages also transform electrical energy into chemical and they have a much faster response if compared to H_2 systems, but they tend to be very expensive and suitable only for small time-shifts like PHS and CAES, where the H_2 storage systems are not ideal.

A good way to take advantage of H_2 storage is to respond to seasonal time-shift. The idea is to store energy during the summer season when the daylight is available for more hours so that PV panels for example produce at their peak and then release this energy during the winter season when the daylight of a day is much shorter. This behaviour is further encouraged if the electricity demand profile of a year is analysed: in fact during the warm seasons less energy is required compared to the cold seasons.

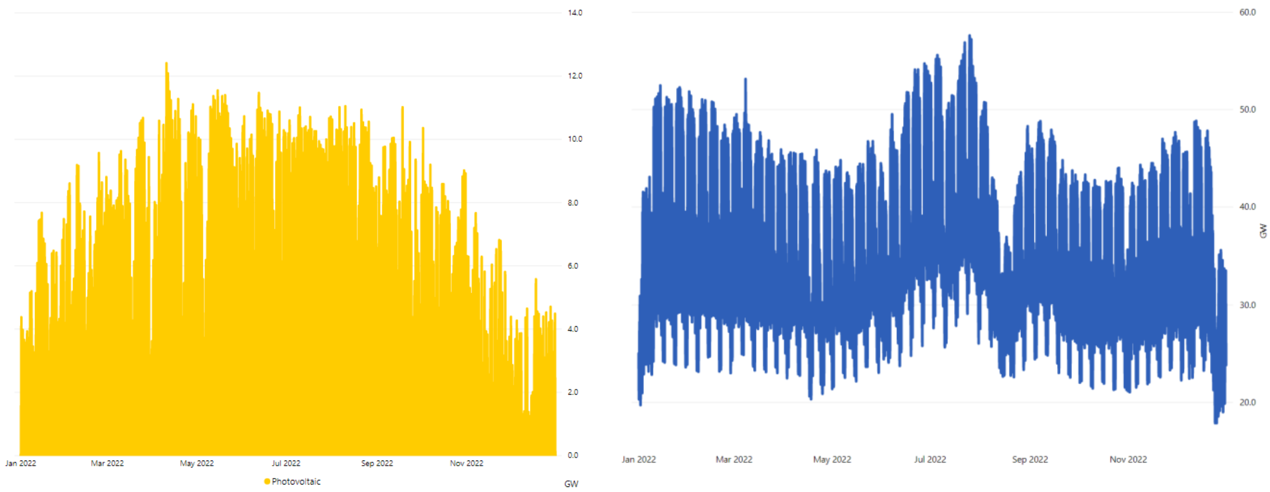


Figure 0-2: Photovoltaic and Total Load Curve in 2022 (GWh)

In order to cover the energy unbalance, a great amount of hydrogen is needed so the point becomes where and how to store it. A suitable way that is being studied is Underground Hydrogen Storage (UHS) in depleted gas reservoirs and it represents the macro-topic of this thesis.

First of all, to demonstrate the viability and effectiveness of UHS, a variety of factors need to be investigated [3]: the retention of gas inside the reservoir, the stability under fatigue stress, the material integrity and the reactive transport. Focusing on the reactive transport there are four macro-areas that have to be studied: thermodynamics, diffusion and hydrodynamics effects, geochemistry effects, and finally biochemistry and biodynamics. This thesis starts from the evaluation of biochemistry and biodynamic effects impact on a real depleted gas field operated as an H_2 storage plant and further analyses the response of this system to realistic H_2 supply and demand scenarios based on future energy systems evolution projections.

An overview of the various topics addressed in each chapter is reported below:

- Chapter 1: Hydrogen and energy transition
  Here a short introduction on how Hydrogen as an energy vector can be produced, utilized, and stored is given. Then a specific insight is dedicated to

underground storage facilities that can be divided into: lined hard rock caverns, salt caverns, depleted gas fields and aquifer. For each technology the main peculiarities and the technological development are presented.

- Chapter 2: Literature Review on related projects
  Here a literature review on hydrogen related projects, separated in the four different technologies of Underground Hydrogen Storage is given: each project is presented with its up to date development and scientific data that were publicly shared

- Chapter 3: Description of the depleted gas field and biological activity modelling
  Here the main properties of the depleted gas field under investigation and an overview of the microbial activity is given. Then the simulators that were used together with possible alternatives are presented and the decision making behind the simulators choice is illustrated.

- Chapter 4: Case Study A - Effects of methanogens archaea on UHS
  The 1st case study focuses on the impact of Methanogenic Archaea on H_2 loss using simulations realized with STARS. The sensitivity analysis reported regard: the Cushion Gas molecule chosen, and the evaluation of the impact of different initial amount of carbon dioxide present in the reservoir.

- Chapter 5: Case Study B: Realistic Energy Scenarios and Applications for UHS
  The 2nd case study changes the focus from the evaluation of biological activity to the analysis of a realistic a H_2 storage in a depleted gas field. Also in this case sensitivity analysis were done and involved: molecule and amount of Cushion Gas injected, Number of wells, definition of different operational schedules and their impact on the storage plant evolution.

- Chapter 6: Conclusions and Further Developments
  Here all the results presented in the previous chapters are summarized and commented. Starting from there, possible future developments are suggested.

1 Hydrogen for energy transition

European and global transition to an overall decarbonized energy system is happening. A reasonable starting point to analyse it, may be the Conference of the Parties (COP21) where lot of countries have signed and ratified the Paris agreement (2015) to keep global warming "well below 2 degrees Celsius above preindustrial levels, and to pursue efforts to limit the temperature increase even further to 1.5 degrees Celsius." [4]

Since that year the commitment to achieve Net Zero GHG emissions by 2050 was taken by new nations and re-enforced by the old ones recently at COP 27 that was held after the global energy crisis sparked by Russia invasion of Ukraine.

This chapter aims to provide an overview of the role that hydrogen might play in the energy transition, then it will investigate UHS options.

1.1. Can Hydrogen substitute Natural Gas?

Hydrogen is sometimes thought as a cleaner substitute of Natural gas (NG) since the applications for which they're used and the location, including the subsurface formations, in which they can be stored are similar. Anyway, some differences between the two gases have to be underlined to point out challenges and opportunities of such substitution for the industry sector.

Nowadays natural gas is stored underground with a capacity of 10% with respect to the global demand. [1] Thanks to these storages, seasonal discrepancies in the global demand, mainly due to heating, plus flexibility requirements can be tackled.

If hydrogen will be able to develop similarly, a key driver will be the availability of renewable-based electricity generation. Presented as a challenge, this might become an opportunity since this storage sites would be spread in many nations providing energy and gas security in case of conflicts like the Russia – Ukraine war that we all have experienced.

Focusing on the technical differences, the main problems that may arise with respect to NG are:

- hydrogen has a higher diffusion coefficient, this makes it more prone to leakage and dispersion inside a reservoir

- hydrogen can interact more with reservoir minerals, this may compromise some reservoir properties like permeability and porosity (geochemical issue)
- hydrogen can function as an electron donor to some microbial processes like methanogenesis, sulfate reduction, acetogenesis and iron reduction (biochemical issue).

In order to address all these technical difficulties a multidisciplinary approach is required including knowledge on reservoir engineering, biochemistry and geochemistry.

Finally, there are two more differences between H_2 and NG that are crucial when a transition to a carbon neutral energy scenario is under discussion:

1. H_2 combustion or RedOx reactions do not emit any GHG while NG oxidation always results in CO_2 production that have to be managed through Carbon Capture Utilization and Storage (CCUS) or other processes
2. H_2 have to be produced through chemical reactions starting from other molecules, i.e. energy vector, while NG can be extracted from subsurface fields implying a much less energy intensive operation, i.e. energy source

The two considerations gain relevance when the concepts of Electrification and Fuel-Switching are under investigation. Let's start by considering how H_2 is produced.

The newest and under development process is Electrolysis of water; here a strong penetration of renewable energy, hence electrification, is mandatory. During over-production periods some extra-electricity would be sent to electrolysers. These systems use electricity to separate water into hydrogen and oxygen as pure products:

$$\text{Global Reaction: } H_2O \rightarrow H_2 + \frac{1}{2}O_2 \tag{1.1}$$

What makes this process different from a normal combustion is that this reaction occurs partially and in different places:

$$\text{Anode Reaction: } H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \tag{1.2}$$

$$\text{Cathode Reaction: } 2H^+ + 2e^- \rightarrow H_2 \tag{1.3}$$

The reactions (1.2) and (1.3) would not happen spontaneously and require electric energy to be activated and sustained.

Another well-developed process to produce hydrogen is Steam Reforming; here methane (CH_4) and heat are the main energy sources required by the endothermic reaction:

$$\text{Steam Reforming (SR): } CH_4 + H_2O \rightarrow CO + 3H_2 \tag{1.4}$$

$$\Delta H_0^R = 206 \frac{kJ}{mol}$$

The final product of this reaction (H_2 + CO) is called syngas, a valuable gas thanks to its wide range of applications and the possibility to further process it to obtain different chemical products like methanol. Another reaction that usually takes place together with SR is:

$$\text{Water Gas Shift (WGS): } H_2O + CO \rightarrow H_2 + CO_2 \quad (1.5)$$

$$\Delta H_0^R = -41 \frac{kJ}{mol}$$

This reaction can be useful since it's exothermic (releases heat that can be absorbed by steam reforming) and can modulate the amount of H_2 with respect to CO that is usually monitored by the module M.

$$M = \frac{V_{H_2} - V_{CO_2}}{V_{CO_2} + V_{CO}} \quad (1.6)$$

$V_{(i)}$: volumetric flowrate of the i-component in a stream

No matter the final application, from the reactions mentioned before it's clear that some CO_2 and CO is going to be present in the production stream together with H_2.

This method is nowadays the main way in which H_2 is produced and is labeled as grey; to improve it and get to zero-/low- CO_2 emissions a carbon capture section has to be considered inside the process (now labeled as blue) making it more complex and expensive but at the same time removing almost completely the GHG emissions.

Once the processes of hydrogen production have been considered it's worth to focus on how it could be utilized. The main concepts under discussion are:

1. Fuel-Switching or Direct Use: in which H_2 is utilized directly by the hard to abate sectors that require heat or H_2 itself and cannot be electrified. POWER-to-GAS logic
2. Conversion to Electricity: where H_2 is used to produce electrical energy when needed by the grid or the final users in place. This might happen once Electrification via strong renewables penetration is achieved and the time-shift driver becomes more relevant than the overall efficiency of the conversion

process of electrical energy into hydrogen back to electricity. POWER-to-GAS-to-POWER logic

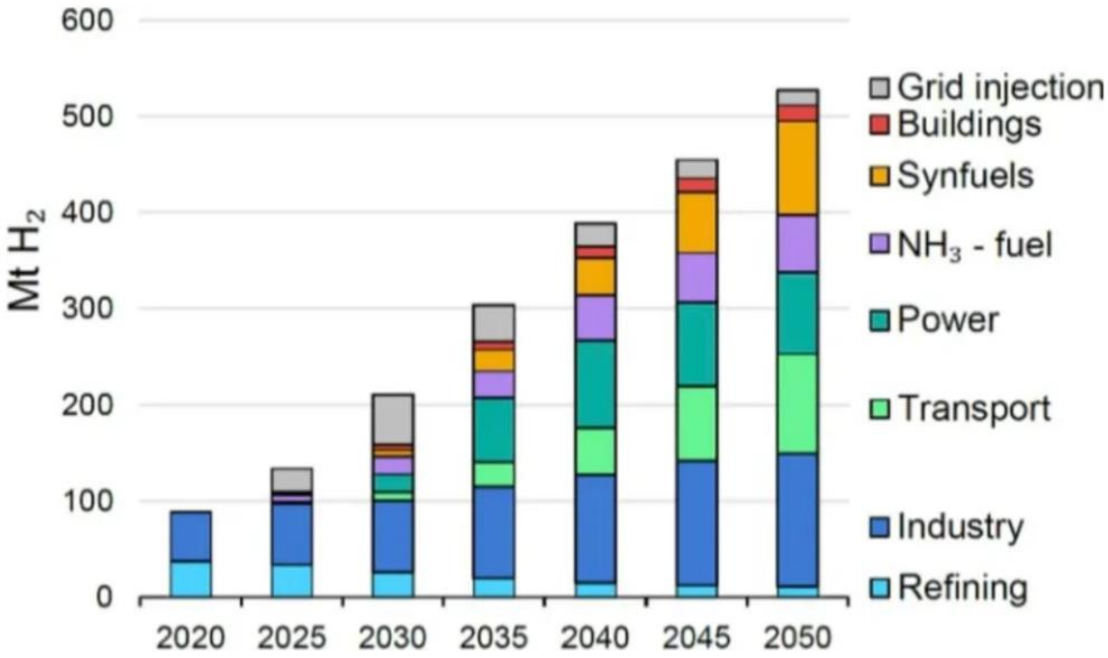


Figure 1-1: Hydrogen projected development in different industrial sector

Now, looking at the increasing hydrogen demand projection made by IEA (Figure 1-1) during 2021 and the different sectors that are going to be involved together with the different ways in which hydrogen can be produced, it seems possible for H_2 to substitute NG. Nevertheless, for this projections to occur, strong investments have to happen both on clean hydrogen technologies and renewable energy production systems considering that of the overall 70 Mt of H_2 produced in 2019, 76% came from NG, 22% from Coal and only roughly 2% from H_2O Electrolysis. [5]

1.2. Underground hydrogen storage

Given UHS as a viable technology to store large amount of energy for long periods it's time to get deeper into possibilities and mechanisms involved. As mentioned before, hydrogen can be compressed and stored subsurface in almost the same sites as natural gas. The most important ones are lined rock caverns, salt caverns, aquifers and depleted gas (or oil) reservoirs.

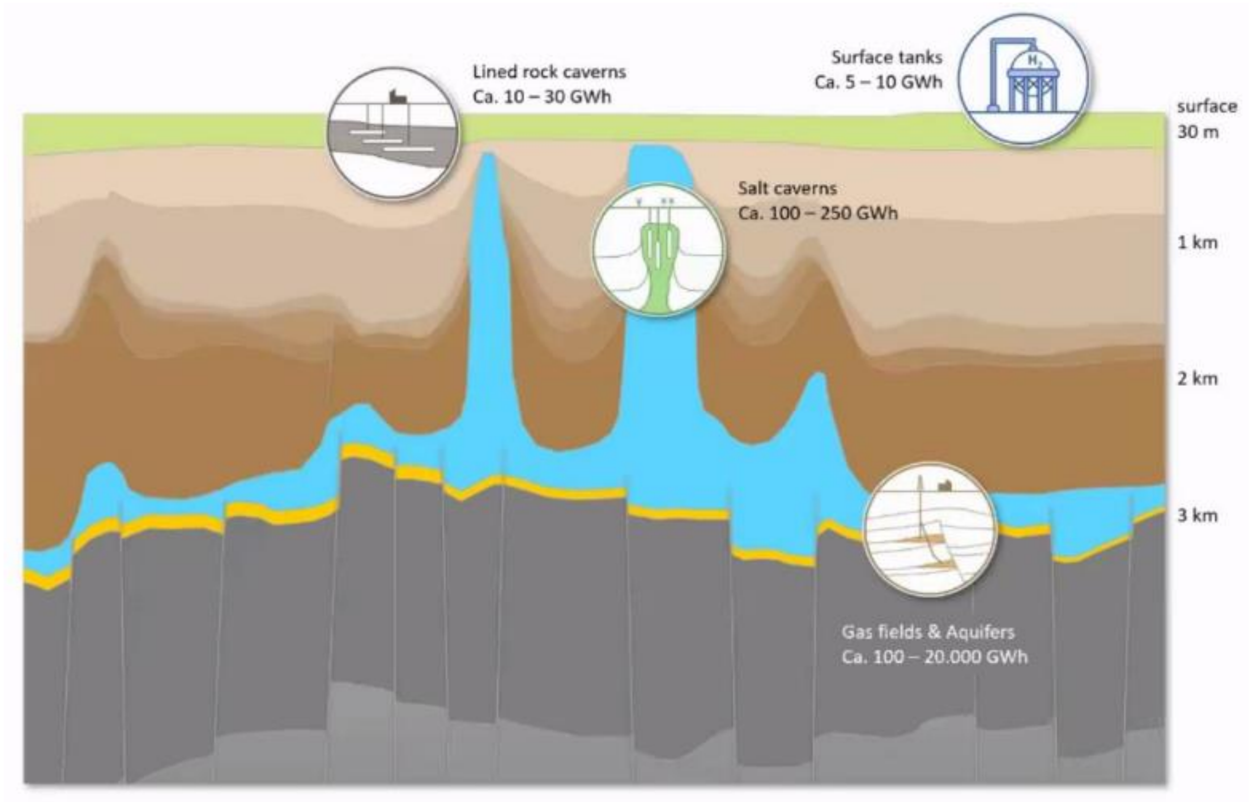


Figure 1-2: Different Underground Hydrogen Storage (UHS) options

These options if compared to the alternative way to store H_2 i.e. surface tanks, present many advantages in terms of:

- Capacity, as shown in Figure 1-2
- Lower costs, since underground sites are frequently already in use from previous operations, hence some components may be recycled, plus there is no need for high pressurization and strong refrigeration plants with at the end a thermally insulated tank to keep hydrogen in liquid phase
  safety, thanks to the geological formation seal, even if investigation on its stability and possible leakage has to be done for each site specifically

Table 1-1: Underground Hydrogen Storage Options Relevant Values [1]

	Lined Hard Rock Cavern	Salt Cavern	Aquifer	Depleted Gas Field
Specific Investment	High	Medium	Low	Low
Levelised Cost of Storage	Medium	Low	Medium	Medium
Cushion Gas *	10-20%	25-35%	50-70%	45-60%
Capacity	Small	Medium	Large	Large
Annual Cycles	Multiple	Multiple	Few	Few
Geographic Availability	Abundant	Limited	Variable	Variable

* Cushion Gas is an amount of gas required as permanent inventory in a storage facility. Its goal is to maintain sufficient pressure in the storage to meet withdrawal demands at high rate, even at low storage levels. This represents a big upfront investment and research have been conducted on the molecules that can be used and the impact of their mixing with hydrogen in order to minimize the impact of this expense. For instance, in this thesis regarding a depleted gas field a sensitivity analysis is conducted by considering H_2, CH_4 and CO_2 as possible alternatives and results would be presented in Chapter 4 and 5.

At first from Table 1-1, it appears that salt caverns are the best option available since they require the lowest amount of cushion gas and they are able to guarantee multiple cycles per year bringing down the levelized cost of storage to the minimum one if compared to others. Anyway their low geographical availability together with the importance of the location constrain for the site to be close to the renewable energy production hubs may strongly limit their spread. A promising alternative is represented by depleted gas reservoirs that have higher capacity and lower cost of investment since they have already lot of infrastructure built around them from their previous operations. Still, the greater amount of cushion gas required and the fewer cycles available per year are downgrades that have to be taken into account. Regarding aquifers and lined rock caverns their effectiveness is still under research. [6]

1.2.1. Lined hard rock caverns

Lined hard rock caverns have been used for storing Liquefied Natural Gas (LNG) and crude oil in the past. Nowadays there is interest to adapt this technology to liquid storage of hydrogen, unfortunately though a containment system similar to above-ground tanks would be required loosing partially the advantage of going underground. Another possibility is to store hydrogen as a compressed gas (100-250 bar) [1] utilizing a liner to improve rock cavern rigidity.

Recently in Sweden a demonstration project first of its kind named HYBRIT was started with an available volume of 100 m^3 and it's expected to run until 2024. At full scale it might get to 100 000 m^3 corresponding to almost 60 GWh of H_2 energy. [7]

1.2.2. Salt caverns

Salt caverns are built by pumping and re-circulating water into underground salt deposit in order to partially dissolve it and create volume capacity for gas storage after the water drainage operation. They are the oldest technology for UHS since the first plants have been running since 1972 in Teesside, UK, Depth: 350-400 m, Total Capacity: 25 GWh. Nowadays the technology has strongly developed and the largest plant in operation is at Spindletop, USA and is capable of storing 274 GWh_{LHV} on H_2 since 2016. [8]

Physically and chemically, salt caverns present strong advantages with respect to their competitors:

- they are very gas-tight, so the overall leakage is under 0.01% of the total amount stored per year [6]
- the salty environment inhibits bacterial activity so hydrogen transformation into other gases isn't an issue
- they can support fast-cycling operation, giving the possibility to inject and withdraw high amount of gas also on monthly basis. Even if research on their integrity when operated in such conditions needs to be done.

Nevertheless, the technology presents the drawback of cushion gas, as reported in Table 1-1 approximately one third of the total gas inventory cannot be withdrawn. Given the advantages of salt caverns and the strong need of UHS in future decarbonised scenarios, lot of projects and pilot plants have been launched and are planned.

Table 1-2: Existing and planned Hydrogen storage facilities for salt caverns

Project Name	**Location**	Start	**Status**	**Capacity (GWh)**
Teesside	UK	1972	Operational	27
Moss Bluff	US	2007	Operational	125
Spindletop	US	2016	Operational	278
Clemens Dome	US	1983	Operational	82
Zuidwending (Hystock)	The Netherlands	2027	Feasibility Study	165 (per cav., up to 4 cav.)
Rüdersdorf	Germany	2022	Under Construction	0.2
Hypster	France	2023	Engineering Study	0.07-1.5
HyGèo	France	2027	Concept	1.5
HySecure	UK	mid-2020s	Concept	40
Energiepark Bad Lauchstadt St.	Germany	2027	Feasibility Study	150
Advanced Clean Energy Storage	US	mid-2020s	Proposed	150 (per cav., up to 100 cav.)
Portland Port	UK	-	Proposed	4.000

Some of the caverns reported in Table 1-2 are designed to operate initially with NG since, as stated by Storengy [9], a NG cavern can store up to 4 times the amount of energy that a H_2 cavern would (mainly because of the low density of H_2 with respect to NG). Nevertheless, in almost every project the capability to store NG-H_2 blending is going to be implemented and some of them i.e. Portland Port (UK) can be completely repurposed to hydrogen in a scenario in which its production through electrolysers would have scaled up.

1.2.3. Depleted gas reservoirs

Gas reservoirs are geological formations made by porous rocks containing gas. They become depleted once the gas inside of them has almost completely been produced and a further exploitation wouldn't bring any additional economic advantage. Once this condition is reached the reservoir can be converted into a gas storage system with the big advantage of having already a lot of geological information and infrastructure built all around for the previous operation requirements. For these reasons storage plants with great capacity could be designed with limited investment and operating costs. In addition to this, some gas is still trapped inside the pores so the technology requires less cushion gas with respect to storage in aquifers. A disadvantage is represented by the mixing between the resident gas and the one for which the storage system is designed. This condition creates, in case of high purity requirements of production streams, the need for up-surface separation components, that can be energy intensive, in order to reach the quality requirement for the produced hydrogen gas.

Nowadays almost the 76% of the natural gas storage relies on depleted gas reservoirs, while research is strongly looking for ways to store hydrogen in blend with NG and later on as a pure component. The reason why these sites gained such a strong interest in the recent period lies in the higher capacity and geographical availability they have in comparison to the more established salt caverns as shown in Table 1-1. Nevertheless. greater challenges are presented since hydrogen is much more difficult to contain with respect to natural gas due to its higher compressibility factor, diffusivity and lower viscosity [10]. Furthermore, the hydrogen molecule is much more reactive and enhance biochemical and geochemical reactions that wouldn't happen with natural gas storage. Another limit, depleted reservoirs have with respect to salt caverns, is the theoretical limited amount of cycles per year they can grant. This makes the storage system suitable for matching seasonal fluctuations between supply and demand of energy together with a security of gas supply increase that revealed to be crucial in the last months in Europe due to the Russia-Ukraine conflict.

Due to all the problematics stated above there are no commercial plants able to store pure hydrogen up to date. Still, both Underground Sun Storage project (Austria) and Hychico project (Argentina) have focused on the idea of storing H_2 together with CO_2 in order to make the facility a huge Underground (bio)-Methanation Reactor (UMR) [11]. This solution grants huge reactor volume, and geothermal heat, which are all crucial aspects in the bio-methanation process. In order to make a UMR plant profitable a deep knowledge on the microbial population together with the brine salinity and reservoir temperature of different sites is mandatory. The methanation itself creates some issues like the biomass grow in the aqueous phase, due to the carbon fixation mechanism, that can lead to bio-clogging effects plus the increase in water saturation itself that can bring down the gas capacity of the system [12]. Anyway, the scenario in which UMR may find practical interest is a strongly hydrogen-based one like the one showed in Figure 1-3. This situation might be difficult to reach in the near future considering the pace at which technologies are developing and becoming cost effective.

More conventional storage studies are the Green Hydrogen @Kinsale (Ireland) and the Storage Hub Italy. Even if they are both in their early stage they seem positive about the possibility to store pure hydrogen in their depleted gas fields. [13]

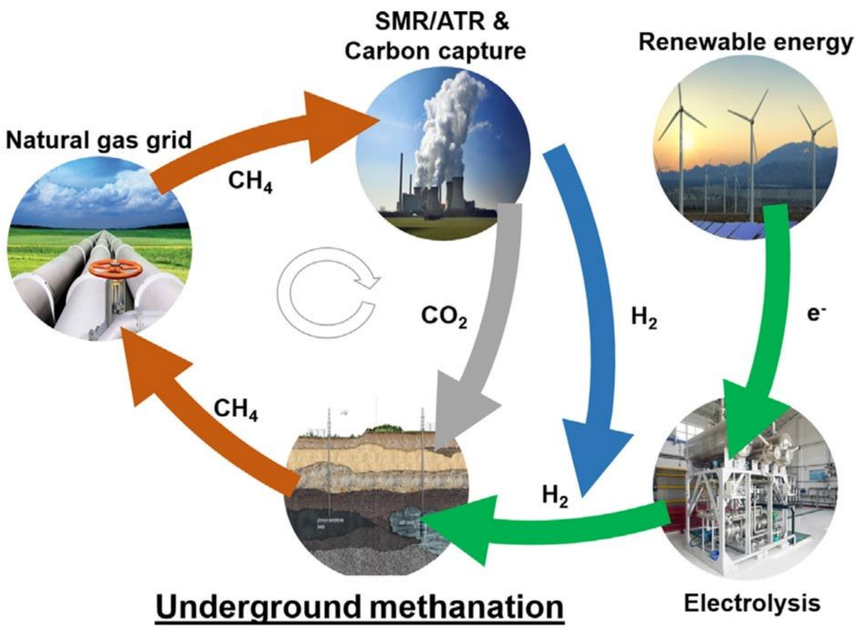


Figure 1-3: Carbon cycle and CO_2 management in a hydrogen-based economy

1.2.4. Aquifers

Aquifers are similar to depleted gas reservoirs: they are porous, permeable sedimentary rock structures saturated with saline water instead of natural gas. To be effective as gas storage systems they must be covered with an impermeable cap rock plus their gas-tightness on all sides has to be evaluated by extensive geological surveys [6]. Nowadays they account for almost the 11% of total underground natural gas storage capacity.

Considering hydrogen, only few plants have tested the possibility to store town gas where H_2 is blended with other components and no pure hydrogen storage plant is commercial or has rather been tested. The main issues are related to hydrogen interaction:

- with rocks, geological and geochemical problem
- with water, difficult to evaluate gas-water contact and equilibrium
- with microorganism, that takes place only in aqueous phase

Aquifers are also the geological formation that requires the largest amount of cushion gas to remain stable and pressurized as shown in Table 1-1. This problem is enhanced with respect to depleted gas reservoir since there isn't any gas in the pores: this condition may also reveal as an advantage since hydrogen production stream is expected to be pure while for depleted gas reservoirs a bit of mixing with the already in place gas is inevitable. The reason why these sites are still of interest is due to their homogeneous geographical spread that makes them the only solution for UHS in some specific world areas.

Looking at the historic data collected from the working storage sites in Europe some information can be extrapolated. For instance the plant in Lobodice has shown a strong hydrogen loss (from 54% to 37% in the overall gas composition) together with the consumption of some carbon monoxide and the increase of methane after a seven months period of injection [6]. This behaviour and the lower pressure observed with respect to the predicted value suggested that methanogens archaea may have been the cause, which was later on confirmed by experimental studies on some fluid samples taken from the reservoir. Some extra considerations are driven by looking at the data collected by the Ketzin plant. Here a strong gas loss was observed in a 20 year span of operation. Proven the gas-tightness and the integrity in the cap-rock the reason for this loss was allocated to biological processes, but considering also the variation in reservoir permeability and gas composition it's safe to assume that extra phenomena have occurred even if they have not been better determined up to date.

2 Literature Review on related projects

Underground Hydrogen Storage plants have attracted lot of interest in the past few decades: many projects have started and many more are going to start in the close future. As stated by the Global Hydrogen Report of 2022 from the International Energy Agency (IEA) [1], strong progress have been done regarding salt caverns storage and they will be crucial in providing flexibility and security of supply in an energy production system with low amount of dispatchable fossil fuel plants.

At the same time the pace of progress on both research and demonstration plants for porous media storage i.e. depleted gas reservoirs and aquifers remained slow. Particular focus should go in the evaluation of residual natural gas effects in depleted fields, storage tightness integrity especially in aquifers and microorganism reactions that may yield contaminants and hydrogen losses. Some of these topics has been addressed in this thesis in Chapter 5 considering a simulation model of a depleted gas reservoir facility in Italy.

In the next section some details about the main projects related to hydrogen storage are summarized.

2.1. Hystories

Hystories, is a two year project founded by the European Union. It started at the beginning of 2021 and recently finished, in December 2022. Due to the high variety of questions it wanted to answer about the feasibility of pure hydrogen storage in porous media eight different work packages (WP) were established. The first four WP were about subsurface technology development: geological (WP1), geochemistry (WP2), biochemistry (WP3) and material corrosion (WP4) challenges have been assessed. The final outcomes are respectively:

- (WP1) a selection criteria to choose H_2 storage sites together with a geological database about sites all around Europe
- (WP2) , (WP3) no public report to date
- (WP4) a protocol to test material behavior to hydrogen contact to get limited to none corrosion and hydrogen embrittlement

The second four WP were about Techno-economic feasibility: Modelling of future European energy system (WP5), (regulation, socio-economic and environmental) Impact Studies (WP6), Ranking of geological sites (WP7), European case studies (WP8). The final outcomes are respectively:

- (WP5) a model able to define different hydrogen ad-hoc storage requirements like: European total capacity [TWh_{LHV}] and equivalent operating cycles per year [1/y] for different scenarios depending on the climate neutrality assumptions considered. This comes with a high number of sensitivity analysis about those assumptions. [14]
- (WP6) a proposal about a suitable regulatory framework
- (WP7) a Life Cycle Assessment (LCA) about a generic underground storage site
- (WP8) no public report to date

2.2. HyUnder

HyUnder, is a project started in 2012 and lasted two years; the countries involved were: Germany, France, UK, Spain, Netherlands and Romania [15]. The main goal of the project was to assess the potential of UHS in salt caverns coupling an energy sector scenario with a high penetration of renewable plants together with transport and industry sectors that were expected to embed almost completely the H_2 demand. Similarly to the case presented before the project was divided into eight Work Packages (WP). The last one, WP8, concluded with an executive summary of the overall project including the up-to-date geological sites information and a promising development plan of UHS in salt caverns complete value chain.

2.3. HyUSPRe

HyUSPRe is a project started in October 2021 and that will finish in December 2023. Its purpose is the evaluation of the potential of implementing large-scale storage of renewable hydrogen in porous reservoirs in Europe to reach a Net-Zero energy system by 2050. This includes the mapping of suitable geological reservoirs and an assessment on the feasibility and pace at which the derived storage plants should be implemented both technologically and economically. The project is once again divided into Work Packages, 7 this time. At first it will address the well-known technical issues and risks regarding storage in porous reservoirs, then it will focus on an economic analysis to enable the decision-making process regarding the development of a portfolio of potential pilot plants. Finally, a regulatory framework will allow to design a possible roadmap for widespread hydrogen storage towards 2050. [16]

2.4. HyStock

HyStock is a company in charge for the underground hydrogen storage in salt caverns in Zuidwending, Netherlands. Nowadays the site is composed of 10 salt caverns, 6 of them are deployed to natural gas storage while the remaining ones are considered for hydrogen storage. Operations have started in April 2021 when a demonstration borehole was first used to store hydrogen: effects on material components and salt walls were minimum while hydrogen quality remained high. After the successful pilot experiment, procedures to get permits to mine the underground were started together with the design of the above-ground installations required to regulate extraction and injections between caverns and pipelines. In 2023 the plan is to have a first cavern to its final shape. Later on the above-ground infrastructures will be completed and connected to the grid by 2026. The first cavern should provide storage services using hydrogen as a cushion gas starting from 2027 while the last three should enter in function one after the other by 2030. [17]

2.5. HyPSTER

HyPSTER is a project launched in January 2021: the objective is to store green hydrogen in the salt cavern of Etrez, nowadays the largest cavern in use for natural gas storage in France. [18] The project is carried on by ESK GMBH, ARMINES-Ecole Polytechnique, Ineris, AXELERA, Element Energy, Storengy and INOVYN. It will be the first plant to store green hydrogen in France since another task of the project is the construction of an electrolyser unit close to the cavern. It's expected to reach the experimentation phase during 2023. The green hydrogen storage main purposes will be:

- Decarbonization of industrial plants switching from grey to green hydrogen
- Distribution to refuelling stations to enable green mobility

2.6. H2STORE and HyINTEGER

H2STORE is a project completed between 2012 and 2015 by a group of universities including: University of Jena, Clausthal University of Technology, GFZ Potsdam and University of Lorraine. The aim of the project was to assess the feasibility of hydrogen storage in porous medium using both numerical simulations and laboratory tests. The project was divided into six sub-projects to investigate in depth mineralogical, geochemical, biochemical and sedimentological issues. The final conclusions can be found here [19].

HyINTEGER started in 2016 and finished in 2019: it is the follow-up project of H2STORE. The University of Mainz entered in the project with the ones mentioned in H2STORE; further investigation was conducted on the same subjects stated before, plus a branch on the effect of hydrogen storage on technical components was opened with particular interest in corrosion phenomena.

2.7. Hychico and Underground Sun Storage

Hychico is a project started in 2010 in Diadema, Argentina. The first pilot test wanted to evaluate the gas tightness and behaviour of the depleted reservoir facility, where a mix between hydrogen and natural gas was initially stored. Later on the project entered in the HyUnder program where further test were conducted and finally in 2014 the approval of the environmental impact assessment was obtained. After one year a specifically designed hydrogen pipeline was constructed and the first results presented at the World Hydrogen Energy Conference in Spain. From 2016 the site was converted to a green methane production plant i.e. an UMR described in Section 1.2.3. Since that time the microbiological campaign and all the correlated activities went on to assess the profitability of green methane production. [20]

Underground Sun Storage is a project conducted in Austria by the company RAG together with Montan University Leoben, University of Natural Resources and Life Science Vienna, Johannes Kepler University Linz, VERBUND AG and Axiom Angewandte Prozesstechnik GmbH from 2012 to 2017. The programme started with the objective of demonstrating the possibility to store increasing amount of hydrogen blended with natural gas in porous geological formations. The in-situ tests experiments gave positive results with a hydrogen concentration up to 20%. [11]
The project got to a second phase with the name Underground Sun Storage 2030 where the activity is proceeding to give insights about 100% hydrogen storage and about green methane production through the already mention UMR concept.

3 Depleted gas field description and biological activity modelling

3.1. Field Overview

Here a geological characterization of the depleted gas field where hydrogen storage was analysed is given. The Nissa field is characterized by a sandstone lithology with claystone intercalations located in a turbiditic depositional environment; the structure is a not-faulted anticline and it's divided on four different levels described different petrophysical properties. The gas in place initial composition is assumed to be a 99% molar fraction of methane and 1% of CO_2. The simulations carried out in this thesis focused mainly on level L3 and on sub-horizontal sectors of it depending on the software in use and on the phenomena that wanted to be studied. The layer based petrophysical properties are listed in Table 3-1. Historical gas production was taken into account to properly capture the reservoir response to a Hydrogen storage operational scenario.

Table 3-1: Petrophysical properties of Nissa field

LEVEL	Φ %	SWi %	Sgr %	K md	GWC m slm	GOIP GSm³	SBHP bar
L1	24,0	33,2	15	60	3060	12.4	337
L2	20,8	41,5	15	50	3185	10.5	356
L3	20,5	38,2	15	50	3225	8.5	362
L4	20,8	43,3	18	2	3807	3.8	504

The Nissa field is surrounded by an aquifer as showed in Figure 3-1 and its influx in the reservoir proved quite strong for level L3 and has been analysed in the operational scenario simulations.

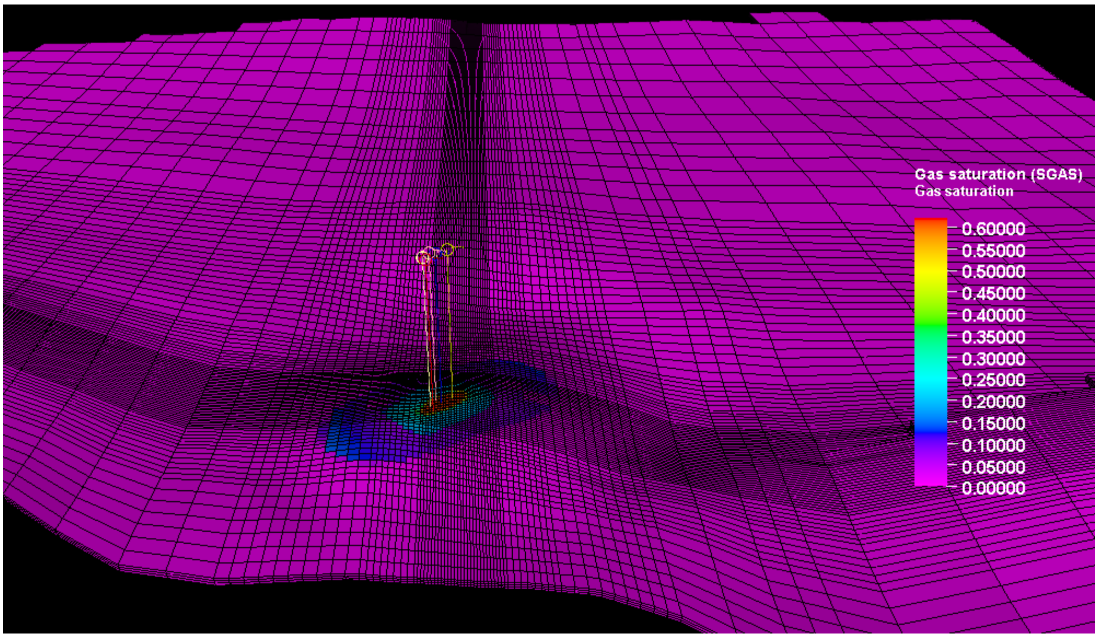


Figure 3-1: Gas Saturation for level L3

Figure 3-1 also highlights the gas saturation region of the level when it was first discovered in the 1970s while Figure 3-2 shows historical pressure highlighting the operation period up to the early 2000s and later on an increase in the pressure level mainly caused by the aquifer push around the gas region. From the 2020s it is showed how a cycling operation hydrogen storage would affect the same parameters. Up to date the Nissa field in stand-by and ready to re-start operations. Many studies were done by ENI on its possibility to become a CO_2 sequestration field to serve the near industrial areas or to operate as an H_2 storage plant thanks to its proximity to a projected off-shore wind farm plant that should become operative in the next few years.

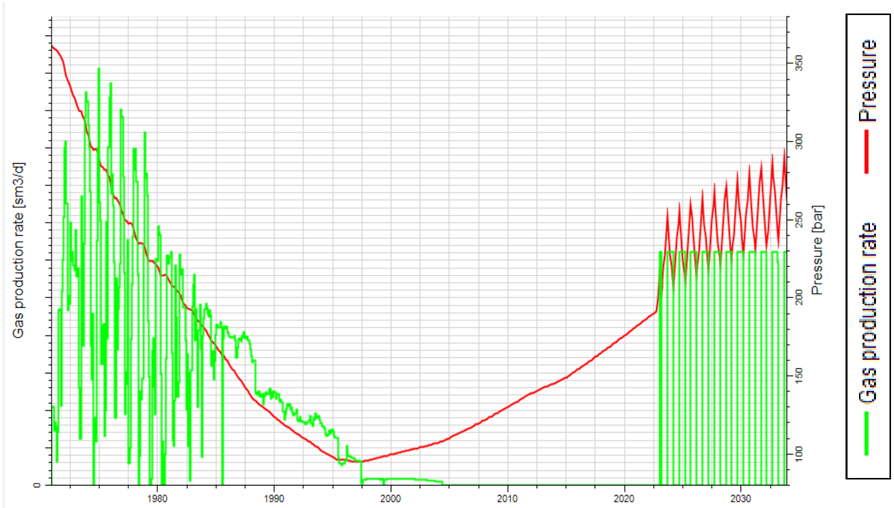


Figure 3-2: Historical Pressure and Gas Production Rate Data

3.2. Biological activity

Among the different challenges correlated to H_2 storage in porous media one of the more relevant is the proliferation of microorganism and their interaction with hydrogen. In particular, archaea and bacteria can use hydrogen to proliferate via bio-chemical reactions causing both hydrogen loss and production of undesired pollutants. It has to be pointed out though, that the survival and proliferation of such microorganism may depend on the conditions of UHS plants (temperature, pressure, pH values and salts presence). One of the objective of this work is the understanding of the impact of this losses, being depleted gas fields one of the most prone sub-surface storage options to present microbial activity.

3.2.1. Microbial reactions analysis

According to the most recent studies on underground microbial activity there are four hydrogenotrophic species that could be relevant during UHS: methanogens, acetogens, sulphate reducers and ferric reducers [5]. Their metabolic reaction differs depending on the electron acceptor they interact with:

- Methanogenic Archaea (M): $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ (3.1)
- Homo-acetogenic Archaea (A): $2CO_2 + 4H_2 \rightarrow CH_3OOH + 2H_2O$ (3.2)
- Sulphate-reducing Bacteria (SRB): $SO_4^{2-} + 5H_2 \rightarrow H_2S + 4H_2O$ (3.3)
- Iron (III)-reducing Bacteria (IRB): $3Fe_2^{III}O_3 + H_2 \rightarrow 2Fe_3^{II}O_4 + H_2O$ (3.4)

Among all the four mentioned reactions only the Methanogenic Archaea reaction was modelled inside the software and these are the reasons of this choice.

The M and A reactions both require CO_2 which can be found underground in the gas composition and in carbonaceous reservoir rocks depending on the geological characterization of the reservoir. It has already been underlined in literature that with the possibility of running both the equation the methanogenesis proliferation occurs much faster and outcompete the homo-acetogenesis [8], hence in the modelling framework only the first reaction was considered.

The SRB reaction requires sulphate to be present: the component can be found in oxidated form dissolved in water and in mineral from depending on reservoir geological characterization. For the specific facility in study no detailed information were available so, as a preliminary analysis, the losses due to these bacteria has been neglected. This is true also for the IRB reaction that once again requires data on the mineral's presence and distribution across the reservoir. It is true that the impact of both this reactions on total hydrogen loss was found to be negligible in similar studies, nevertheless a correct evaluation of H_2S amount in the production stream is an interesting further development for the project.

3.2.2. Microbial growth Chemical & Mathematical description

Microorganism mass is divided approximately in water 80% and organic material 20% [8], for this reason they can survive and proliferate only in aqueous phase. They reproduce through dichotomy of cells; this process occurs only when the original microbial cell is ready meaning that the metabolic reactions of respiration and nutrition have already took place contemporary. The respiration process consists in the activation of a RedOx reaction within the microorganism and hydrogen takes the role of electric donor giving the energy necessary to sustain the reaction. This is the hydrogenotrophic part of the metabolism and is responsible for the evolution of H_2 into other chemical species. In the meantime the nutrition process is developing: here mass and dimensions of the bacterial cell are increased thanks to the carbon fixation mechanism that require an external organic carbon source like CO_2.

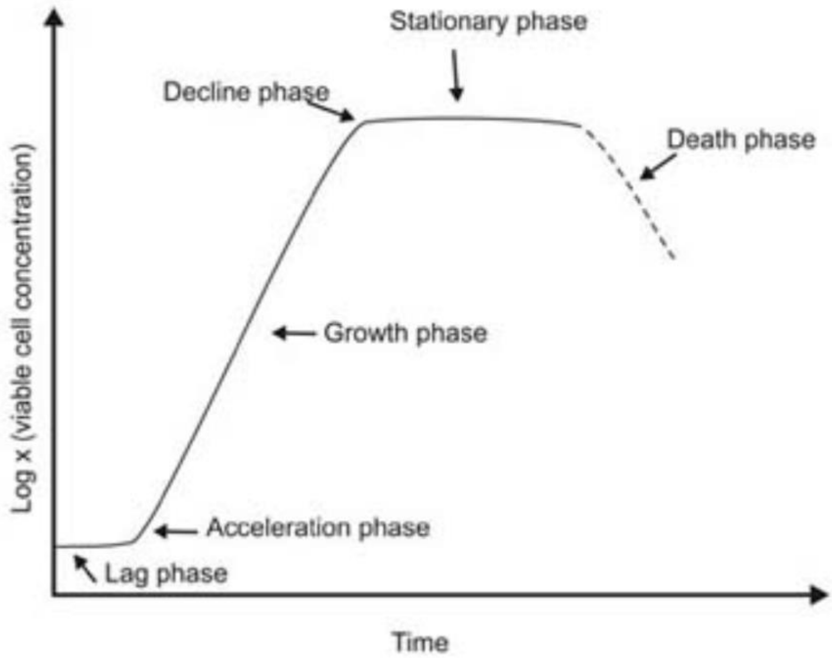


Figure 3-3: Microorganism Proliferation in a Batch culture laboratory experiment

The growth behaviour of different microbial species has been investigated deeply in laboratories using batch culture experiments. Figure 3-3 shows the number of microorganisms in logarithmic scale in function of time: here different phases can be distinguished.

1. The lag phase is a period in which there is no proliferation since adjustment to external conditions set is required: it might last from few minutes to several hours in laboratory, but time can increase up to years in sub-surface environmental conditions
2. The acceleration phase in which the proliferation starts but it has not reached yet the regime: this phase was introduced specifically by Monod
3. The exponential growth phase that appears as a line in the logarithmic scale is when the proliferation occurs at its maximum rate: the time span of this phase can last up to 100 years.
4. The decline phase in which one between the energy source (hydrogen) or the carbon source for fixation (carbon dioxide) is starting to be poorly distributed
5. The stationary phase during which no net growth is occurring since the proliferation rate is matched by the decay
6. The decay phase in which the overall death of microbial cells overcomes the proliferation reaching an exponential decline condition

Starting from these laboratory experiments many mathematical models have been developed. In this work the Double Monod model was adopted.

$$\psi^{growth} = \psi^{growth}_{max} \left(\frac{x^{H_2}}{\alpha_1 + x^{H_2}} \; \frac{x^{CO_2}}{\alpha_2 + x^{CO_2}} \right) \tag{3.5}$$

This model is widely utilized in environmental engineering applications and since the focus of the thesis was to capture the growth mechanism of microorganism to evaluate H_2 losses and pollutant production only the first four phases of the model were described. It was possible to neglect the death phases without compromising the results since microorganism remain always in aqueous phase and the production stream coming from the well is almost completely gas (with a Water-Gas ratio always kept below 1e-04), hence close to no microorganism would reach the up-surface components. Another important consideration regarding the microbial activity taking place only in aqueous phase is that hydrogen solubility is actually very low; for example if compared to CO_2, the other reactant for the Methanogenic Archaea reaction, the Henry's constant ($\frac{mol}{m^3_{H2O}} Pa$) of the two differ by two orders of magnitude (7.8e-06 for H_2 and 3.3e-04 for CO_2 @ 25°C) [21].

3.2.3. Microbial transport & Physical properties influence

Microbial modelling is not limited to proliferation as also transport of microorganisms may occur. This mechanism is actually very complex to analyse: advection, dispersion, straining and physical filtration all together take place at the same time. However, since microbial life in subsurface formations is mainly organized in biofilms attached to solid rocks surface, the microorganism are almost completely steady, hence such degree of complexity could be neglected in this work.

Reservoir properties, such as pressure, temperature, salinity and pH, have an impact on the microbial activity. The parameter that is influenced by these properties is the amount of H_2 microbial oxidizers and the physical processes involved are: variation in gas-water equilibrium, osmosis and microbial competition.

- Gas-water equilibrium: a decrease in pressure and an increase in temperature would decrease the final solubility value hence decreasing the proliferation that occurs only in aqueous phase
- Osmosis: a mechanism that consist in a spontaneous diffusion movement across a semipermeable membrane (the cell membrane in this case) to balance a molecule concentration between two regions. For this specific case is water flowing in and out from the microorganism depending on the salt concentration, hence salinity and temperature are the parameters to consider. An increase in both value would increase the osmotic pressure of the cell compromising the microorganism survival

- Competition between microorganism depends mainly on the proliferation rate of the different reactions that is specifically influenced by temperature and pressure

Looking at the pH impact it has been found in literature [22] that a value below 7 favours the methanogens over sulphate reducers while for values upper 7.5 the contrary is true.

As a general guideline, microorganisms prefer an environment characterized by low temperatures, low salinities and a neutral pH. So to perform a safe H_2 storage operation, sites with a temperature higher than 50°C and salinity over 100 g/l are preferable. [23] Finally, it is worth mentioning that almost no literature is available on the correlation between specific reservoir properties/conditions and microbial growth evolution so in the modelling framework this aspects were marginally considered.

3.3. Modelling Tools

Two software have been utilized to carry on the thesis simulation: STARS from the CMG group [24] and ECHELON internally developed by ENI. The choice between the two was guided by the aspects that had to be simulated in details. The main reason to use STARS with respect to ECHELON is its capability to model chemical reactions: a crucial aspect in the evaluation of the Methanogenic Archaea impact. There are other simulators able to model underground chemistry like GEM (also developed by CMG [25]) which can also treat the fluid mixture directly with EoS (Equation of States) specified for each component. In this way the software could evaluate the vapour-liquid mixture separation with an almost completely analytic approach while STARS, using the k-values method described in Section 3.3.1, gives results that are correct but not extendable to very different reservoir conditions. The reason why STARS was chosen over GEM is that for this specific microbial proliferation conditions GEM simulations came out with a non-negligible material balance error while STARS never presented this kind of issue. Unfortunately both STARS and GEM do not have the possibility to model exactly the microorganism proliferation chemical reactions. What they both can do, and was done in this thesis, is to tune a Power-Law reaction rate in realistic range of aqueous concentration of reactants and use this type of kinetic description. A different viable solution could have been PHREEQC which is a software able to model specifically microbial biomass growth, unfortunately though it supports only 0D and 1D studies and it was impossible to adapt it to the Nissa field 3D grid description.

Once the focus is shifted from chemical reactions to plant operation description the ECHELON simulator [26] is chosen. This because even if nowadays this software doesn't support underground chemistry ENI has an ambitious program to insert it and to improve this simulator that was initially designed to evaluate gas production schedule of oil and gas facilities to a simulator able to model much more complicated underground situations. Furthermore, with respect to all others software presented before ECHELON is the only one able to manage techno-economic criteria on well operations (i.e. water gas ratio maximum limit) and flexible flowrate schedule tuned on external data presented in Section 5.6. Table 3-2 summarizes the tools each simulator grants to better understand the final choices of STARS and ECHELON.

Table 3-2: Simulators available and their specifics

	ECHELON	STARS	GEM *	PHREEQC
Chemical Reactions	No	Yes	Yes	Yes
Microbial Growth	No	No	No	Yes
3D Grid Modelling	Yes	Yes	Yes	No
Well Description	Yes	Yes	Yes	No
Techno-economic Controls	Yes	No	No	No
Flexible Flowrates	Yes	No	No	No

* GEM has material balance issues for this specific application

3.3.1. STARS simulator

This STARS simulator was used to capture the methanogens proliferation. The software is capable of simulating reservoir evolution during hydrogen storage using:

- Mass Conservation and Darcy's Law
  $\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho v) = 0$ and $q = -\frac{K}{\mu L} \Delta p$ (3.6) (3.7)
- Components Vapour-Liquid Equilibrium through appropriated k-values in input (which depends on the pressure and temperature conditions)
  $k_i = \frac{y_i}{x_i}$ i: component index (3.8)
- Chemical Reactions: using a tuned Power-Law model to represent the rate of any reaction
  $R^{Power-law} = F \prod_{i \in reactant} \hat{c}_k^{\beta_k}$ tuning parameters: F, β_k (3.9)

As stated before the model that was chosen to capture the methanogens proliferation was the one suggested by Monod in its more complete version:

$$R^{Double-Monod} = \psi_{max}^{growth} \frac{\gamma}{Y} \left(\frac{x^{H_2}}{\alpha_1 + x^{H_2}} \frac{x^{CO_2}}{\alpha_2 + x^{CO_2}} \right) \quad (3.10)$$

Unfortunately STARS doesn't support this reaction rate modelling so starting from the work developed in a previous thesis project a new tuning of the parameters cited above was done via equation (3.13) and a satisfying matching between the two representations was reached as depicted in Figure 3-4.

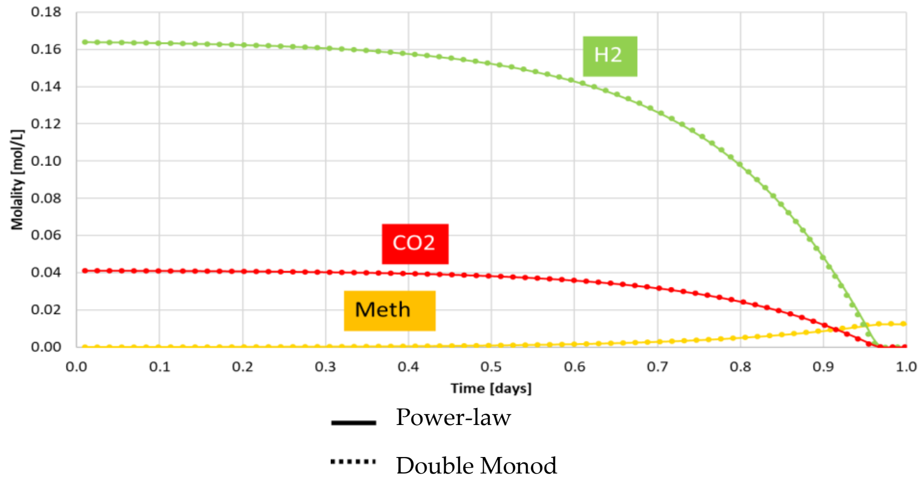


Figure 3-4: Result of Power-law tuning over the Monod model

$$R^{Double-Monod\ approx} = \psi_{max}^{growth}\ \frac{\gamma}{Y}\ \left(\hat{F}\hat{c}_{H_2}^{\beta_{H2}}\hat{c}_{CO_2}^{\beta_{CO2}}\right)k_n n_b \qquad (3.13)$$
$$= F^* c_{H_2}^{\beta_{H2}}\hat{c}_{CO_2}^{\beta_{CO2}}$$

3.3.2. ECHELON simulator

The ECHELON simulator was used to evaluate the reservoir response to a hydrogen storage operation period. The simulator has been developed jointly by Eni and Stone Ridge technology and was initially thought to model oil fields through a black oil logic where families of molecule with similar weight are considered as one single component since the oil composition can be very heterogeneous. For this thesis the compositional version was used: here every component, is simulated separately. In our case two components were included in addition to water, CH_4 and H_2. No CO_2 was considered since this simulator is not able to capture chemical reactions (while is still able to capture all the other features of STARS plus some extra) and the CO_2 initial presence in the reservoir is negligible. The following tecno-economical constrains were assumed:

- Bottom Hole Pressure of Wells (BHP)
  Max value: 360 bar Min value: 90 bar technical limitations
- Water Gas Ratio (WG-ratio)
  Max value: 1e-04 tecno-economic limitation
- Maximum Flowrate per Well

Value: 2% of estimated capacity technical limitation

The focus was to capture hydrogen transport and segregation in a depleted gas field over a decade of cycling storage operation. The operation schedule, given by injection and withdrawal surface flowrate, was also varied to get a more realistic view of the phenomena involved. Particularly relevant in this model framework are the Gravity Forces and the Viscous Forces. Since hydrogen as a much smaller density compared to methane (0.084 kg/m3 H_2 vs 0.651 kg/m3 CH_4 @Sc) [27] [28] the gravity override phenomena should help in keeping the H_2 on top of residual methane in order to minimize contamination of the production stream. A similar difference can be seen also for viscosity (0.0086 cP H_2 vs 0.0107 cP CH_4 @Sc) [27] [28] bringing the ratio between the two values up to 1.24 which means that an instable displacement may occur when hydrogen is inserted in a field where methane is present. Anyway much more challenging displacement are already tackled in industrial applications such as the one involving gas-water where the viscosity ratio is greater than 100.

4 Effects of methanogens archaea on UHS

4.1. General introduction

In order to get a comprehensive view on the H_2 losses due to methanogens in a depleted gas field a sector of the reservoir level described in Section 3 was modelled using STARS. Then a sensitivity analysis on some of the most impacting parameters was carried out to capture their relevance on the final results. The main inputs adopted in the base case are:

- The Grid Dimension: 66x69x3 (i, j, k) – Init. Pore Volume Simulated: 9.002E6 m^3
  This is actually a small section of the overall reservoir and was cut in order to emphasize the behaviour of the gas saturated region with a small part of the aquifer. On the extreme cells specific boundary conditions were given in order to get a rough description of the aquifer outside the grid: this was done to save computational time
- The k-values coefficients of each component
  They are tuned starting from the Henry's constants and are responsible for the distribution of a specific component between the aqueous and the gaseous phase

Table 4-1: k-value coefficients to be inserted in experimental correlation (4.1)

COMPNAME	'WATER'	'CH4'	'H2'	'CO2'	'Bact1'
KV1	0,000E+00	1,034600E+06	8,974119E+04	5,323305E+06	0
KV2	0,000E+00	0,000000E+00	0,000000E+00	0,000000E+00	0
KV3	0,000E+00	0,000000E+00	0,000000E+00	0,000000E+00	0
KV4	0,000	-1032,229	-140,159	-2002,109	1
KV5	0,00	-273,15	-273,15	-273,15	0

$$k_i(p,T) = \left(\frac{kv_{1i}}{p} + kv_{2i} * p + kv_{3i}\right) * EXP\left(\frac{kv_{4i}}{T - kv_{5i}}\right) \quad (4.1)$$

- The physical properties of each component (Water values are 0 since their already inside the simulator by default)

Table 4-2: Molecular Weight (CMM), Critical p and T, Viscosity Coeff. for eq. (4.2)

COMPNAME	'WATER'	'CH4'	'H2'	'CO2'	'Bact1'
CMM	0,000	0,0160430	0,0020159	0,0440100	0
PCRIT	0,00000	46,00155	13,15200	73,76460	0
TCRIT	0,00	-82,55	-239,96	31,05	0
AVISC	0,000E+00	-2,11497E-02	5,235169E-03	3,573556E-02	0
BVISC	0,000000	85,901924	9,876230	182,632273	0

$$\mu_i = avisc_i * EXP\left({bvisc_i}/{T_{abs}}\right) \quad (4.2)$$

- Initial Reservoir Conditions (initial pressure, temperature)
  Initial pressure was chosen considering a realistic value for the production end moment. Here no history operation was modelled since it was not crucial in evaluating methanogens losses and would have largely increased the computational time of each case simulation. Temperature was kept constant: this is a realistic assumption for the reservoir operation time-scale and would not strongly affect the microorganism proliferation

- Chemical Reaction parameters

Table 4-3: Stoichiometric Coeff, Reaction Orders, Aqueous critical concentrations

COMPNAME	'WATER'	'CH4'	'H2'	'CO2'	'Bact1'
R_ORDER	0	0	1,200E-03	3,197E-02	1
STOIC_REAC	0	0	4	1	1
STOIC_PROD	2	1	0	0	1,3
AQ_CRIT_CONC	0	0	1,60480E-01	1,60480E-01	1

Reaction Orders are based on the initial component aqueous concentration
Aqueous critical concentration is specified to maintain numerical stability when the reaction is close to ending the reactants

- Rock-fluid properties
  Initial Gas and Liquid saturation distribution for each grid cell, Critical Gas saturation distribution value in each grid cell, Water-Gas Contact depth value (3229 m) and Critical Water Saturation value (0.382)

- Aqueous Initial Concentrations (mass-weighted) for grid cell

Table 4-4: Well Dimensions and characteristics and Target Surface Flowrate

Radius [m]	Geom Fact	wfrac	Skin Fact	Surface Flowrate [Sm3]
0,108	0,37	1,0	0,0	5,00E+05

- Operational Schedule:
  Total period simulated: 6 months of cushion injection plus 2 years of operation
  Schedule: 6 months of injection and 6 months of production cycles

The parameters used for the sensitivity analysis, presented in the schematic Figure 4.1, were varied once at a time to evaluate their impact on the final outcomes.

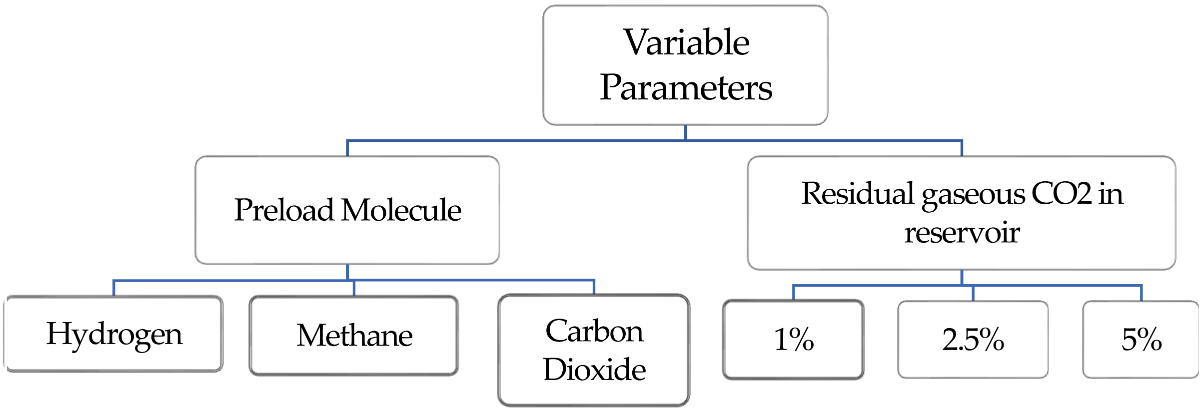


Figure 4-1: Variable Parameters scheme for sensitivity analysis

4.2. Base Case definition & Analysis

In this reference case the Cushion Gas molecule is H_2 itself and the initial amount of CO_2 present in reservoir is 1% (in mole fraction) of the total initial gas composition. This last parameter may vary depending on the field at hand this value was assumed as higher threshold considering typical Italian gas reservoirs.

In order to evaluate the total amount of H_2-loss given by the methanogens proliferation two different cases were compared. The former one shows the reservoir evolution with Methanogenic Archaea reactions active while the latter does not consider the Archaea effects. The main parameter to focus on was the Gas Production Rate Composition, because any change in this parameter between the two cases would show the actual impact of methanogens.

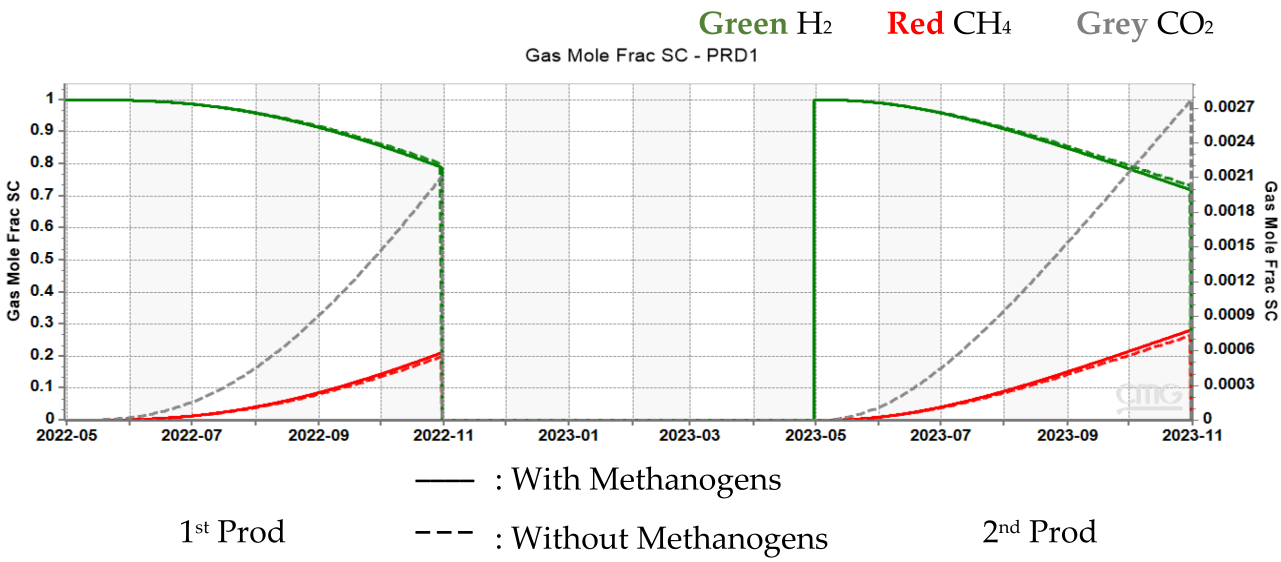


Figure 4-2: Gas Production Rate Composition

By looking at Figure 4-2 it can be immediately seen that the compositions are very similar: however the CO_2 amount is quite different since it is absent when methanogenesis is activated. This difference is emphasized by the variation in y-scale since the maximum value of CO_2 in production stream is up to 0.0027 molar fraction: nevertheless, it's true that this amount would not be emitted in presence of bacteria. This because the methanogenic archaea reaction would consume all the CO_2 close to the hydrogen injecting well, consuming hydrogen and producing CH_4 and water and that's why a small increase in methane and decrease in hydrogen concentration can be seen when archaea are involved. To evaluate the global losses, cumulative values of produced gas stream were considered in both cases and Table 4-5 shows the final result:

Table 4-5: Methanogens losses and Total losses for each cycle and for the 2 years

	Losses due to Methanogens	H_2 Tot Loss
1° cycle	0.301%	6.36%
2° cycle	0.501%	10.61%
Overall	0.401%	8.49%

It can be seen that the loss due to Archaea is very small especially when confronted to the global H_2-loss that takes into account also H_2 distribution and transport in the gas field and the partial mixing process with the initial gas in place. This last process is strongly influenced by the cushion gas molecule chosen as it would be emphasized in Section 4.3. To get a better view on the microorganism impact Figure 4-3 shows the final Methanogenic Archaea concentration distribution and Figure 4-4 catches a specific grid cell in which the proliferation has taken place, is analysed.

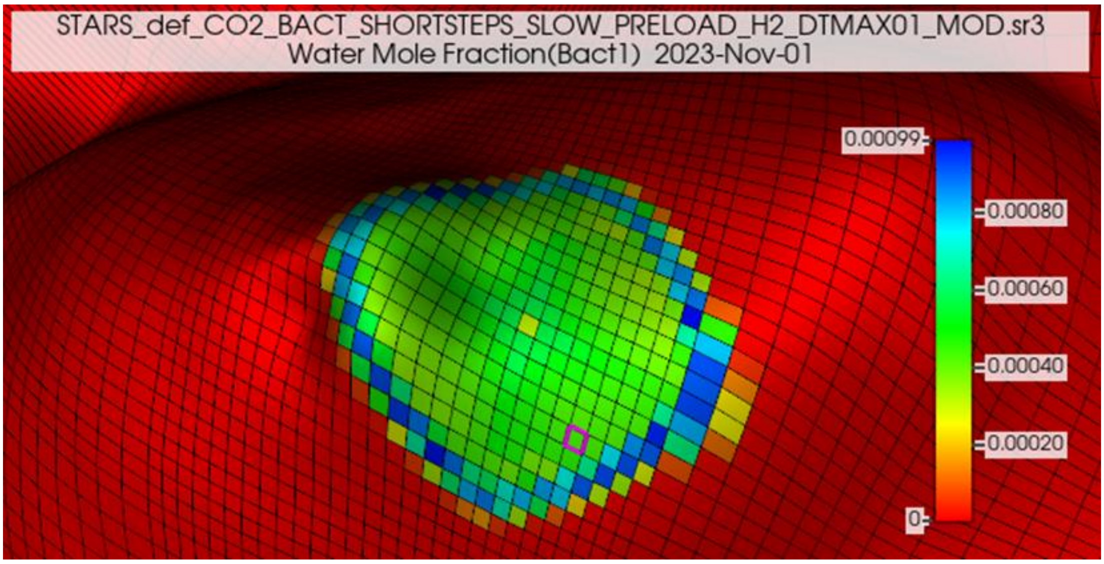


Figure 4-3: Methanogenic Archaea final aqueous concentration distribution

PRELOAD H2 1° INJ H2 1° PROD 2° INJ H2 2° PROD

Figure 4-4: Components aqueous concentration evolution

By looking at the distribution it is possible to notice that the proliferation around the well-developed up to a certain value while at the boundaries the proliferation was able to perpetrate more. This is mainly due by the reactant transport throughout the reservoir during the operations. At the beginning, with the injection of hydrogen as cushion gas, the reactant for methanogenesis are both available so the proliferation will start and reach its limit once the CO_2 aqueous concentration has been completely consumed. This means that additional hydrogen would pass the proliferation region without contributing to the Archaea growth. Nonetheless at the frontier, where CO_2 is still available, bacterial proliferation may occur. In particular during the production period, some of the original CO_2 present in the reservoir areas not yet reached by hydrogen is transported towards the frontier where the proliferation has once again all the reactants and can occur. As highlighted by Figure 4-4 though, the consumption of hydrogen (which results in an equivalent formation of methane) due to this reaction is limited, due to the low availability of CO_2 which acts as a limited reactant, and the overall cycling trend given by the injection/production alternation schedule is maintained

4.3. Methane as Cushion Gas

Here the cushion gas molecule is methane which would represent a smaller fixed cost with respect to hydrogen given the lower price of this gas while the initial CO_2 in reservoir is kept at 1%.

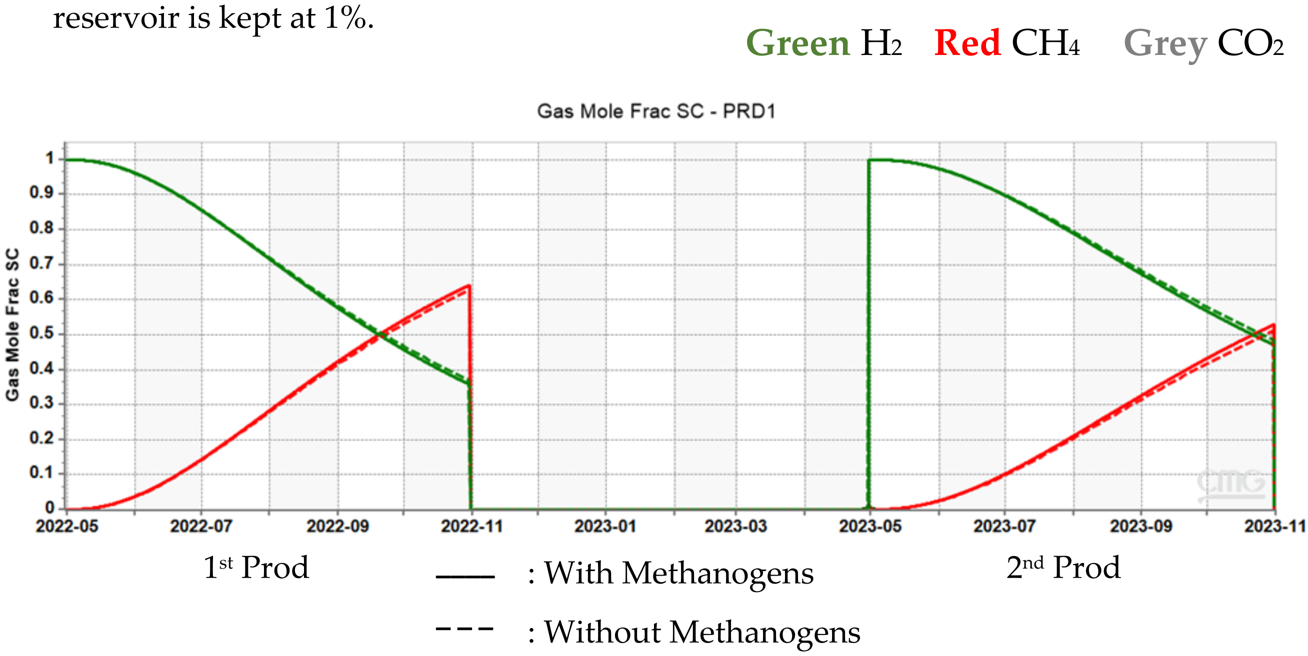


Figure 4-5: Gas Production Rate Composition – Methane as cushion gas

The Gas Production Composition looks quite different from the previous case on absolute values even if the distance between the continuous and the dotted line is still small meaning that the bacterial losses would remain small.

Table 4-6: Methanogens losses and Total losses for each cycle and for the 2 years

	Losses due to Methanogens	H_2 Tot Loss
1° cycle	0,430%	28,820%
2° cycle	0,590%	22,380%
Overall	0,511%	25,600%

In fact, by looking at Table 4-6 there is an almost constant loss due to Methanogens with respect to the Base Case while the H2 global loss is strongly increased mainly because of the mixing between hydrogen and methane that now is working also as a cushion gas so it is going to be more in contact with hydrogen.

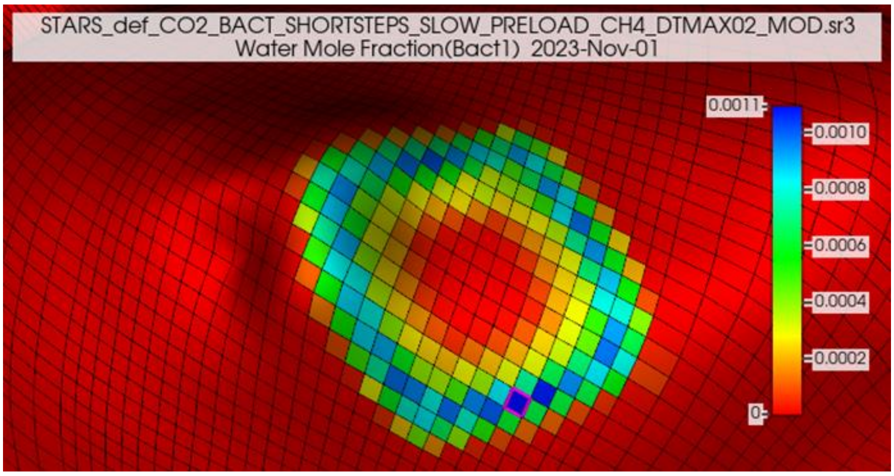


Figure 4-6: Methanogenic Archaea final aqueous concentration distribution

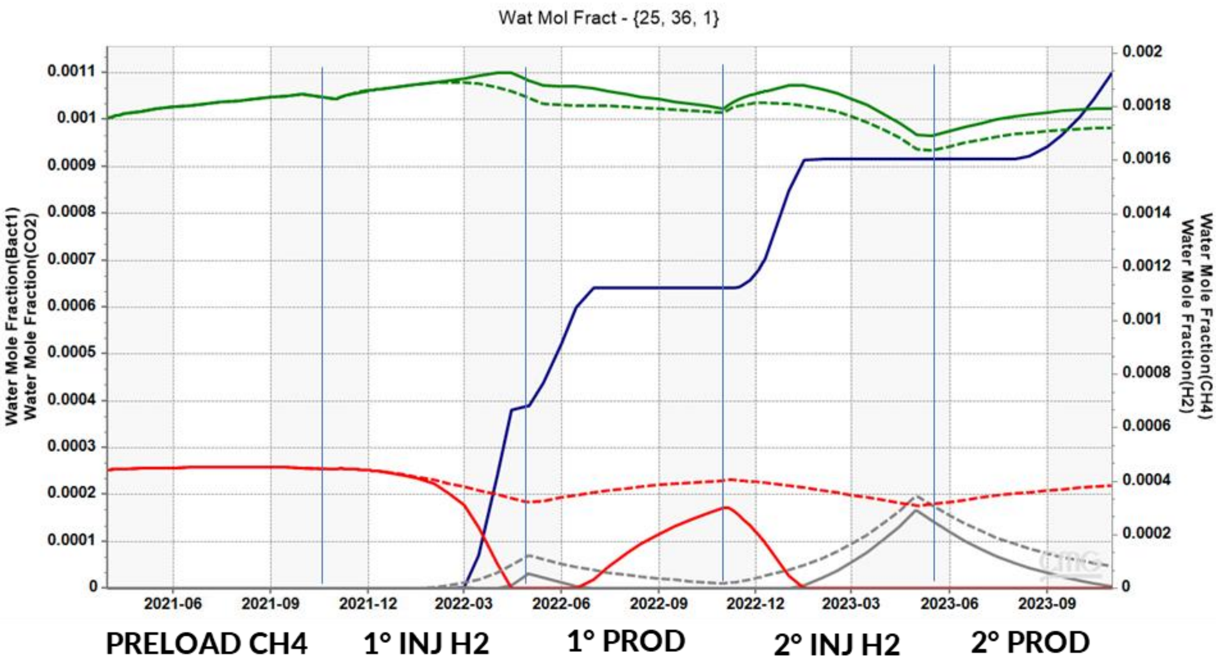


Figure 4-7: Components aqueous concentration evolution

The reservoir proliferation of Methanogenic Archaea in Figure 4-6 shows that something different has happened with respect to the previous case. Here there is a region all around the injection well where the proliferation has not occurred. The explanation lies in the distribution of reactants, since during the methane preload the CO_2 already present in the reservoir is displaced away from the near-well region, so once the hydrogen is injected, no CO_2 is present, hence no carbon fixation is possible so the microorganism proliferation can't occur. Once hydrogen has reached a region where also CO_2 is present the proliferation occurs. Also in this case there is an increase of the archaea at the frontier during production phases where reactants become available, for the same reasons explained before.

The graphic representation in Figure 4-7 of the same cell analysed in the previous case gives other important information. As expected during the cushion gas injection (preload period) no reaction is occurring since no hydrogen molecule is present in reservoir. Then, when hydrogen reaches the cell, the CO_2 consumption occurs. Since the cell is located at the frontier, the proliferation can go on in the various cycles resulting in an higher hydrogen consumption and bacterial growth. In fact by looking at the 1st production phase it can be seen that hydrogen is completely consumed acting as a limiting reactant and letting the CO_2 concentration increase. This mechanism ends when the 2nd injection of hydrogen occurs; this happens because now plenty of hydrogen is coming from the near-well region, it consumes all the CO_2 present in the cell and finally increases its concentration up to the 2nd production phase.

This configuration has showed what happens when the limiting reactant is switched to hydrogen; this phenomenon could be captured thanks to the Double Monod approach that models both H_2 and CO_2 as possible limiting reactant.

4.4. Carbon Dioxide as Cushion Gas

To complete the sensitivity analysis on the cushion gas molecule the CO_2 case is analysed. This particular case is interesting by a tecno-economic point of view since it makes possible to accomplish both CO_2 sequestration and H_2 storage in an unique depleted field. This means that the cushion gas wouldn't represent a fixed cost but an earning instead. The last sentence would be true only if the interaction and mixing of CO_2 and H_2 is limited, hence the Methanogenic Archaea are not present or able to proliferate due to reservoir specific conditions.

Notably, as cited before in Section 1.2.3, there are some ongoing research projects that look at methanogenesis as a desired effect: here the objective of the plant is not to be an H_2 storage facility but to act as huge sub-surface methanogenesis reactor that wants Archaea to enhance methane formation. In this operation scheme it is possible/recommended to inject not only hydrogen but also carbon dioxide that might come both from a different industrial plant or directly from an air sequestration plant to enhance a more sustainable carbon cycle as showed previously in Figure 1-3.

Anyway, in this thesis the depleted gas field is always considered as an H_2 storage plant, this means that by looking at Figure 4-8 it is immediately possible to see that the methanogens proliferation compromises the gas production composition so much that in the vast majority of production period no hydrogen is produced and it's replaced mainly by CH_4 and some CO_2.

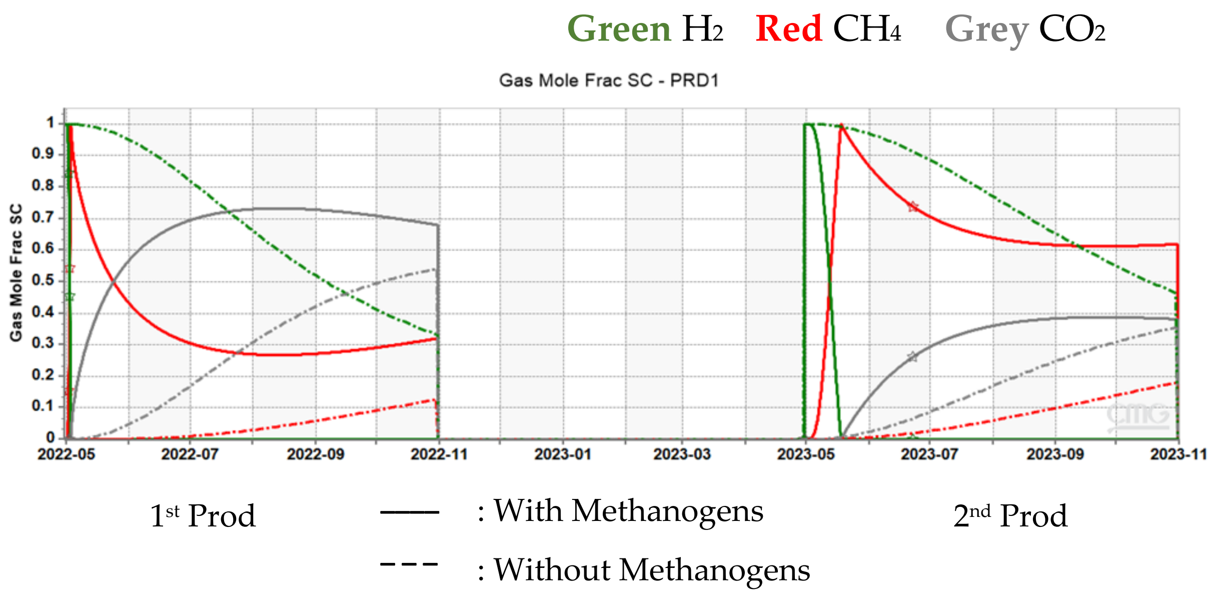


Figure 4-8: Gas Production Rate Composition – Carbon Dioxide as cushion gas

Another aspect worth to mention is the pressure evolution throughout the simulation. In fact when the stars appear in Figure 4-8 it means that the production well has reached is Bottom Hole Pressure Minimum limit and will start to lower the production rate scheduled up to extreme cases in which it could directly close itself. This depressurizing effect can once again be ascribed to the methanogens proliferation, since with that large amount of CO_2 available the reaction can go on, consuming four moles of the injected hydrogen and producing just one mole of CH_4 and two moles of water.

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \tag{3.1}$$

This means that the reaction, even if it occurs in the aqueous phase, is actually decreasing the amount of gas inventory in the reservoir since the equilibrium ratio of specific components in the two phases is kept due to the k-values constrains. In fact, lowering the gas inventory means lowering the reservoir pressure.

4.5. Different Initial Carbon Dioxide amount in reservoir

The last parameter that was varied was the initial amount of CO_2 present in reservoir. The considered values were the 1% case (already seen) and the 2.5% and 5% (mole) fraction in gaseous phase cases. All these different simulations were done with hydrogen as cushion gas molecule.

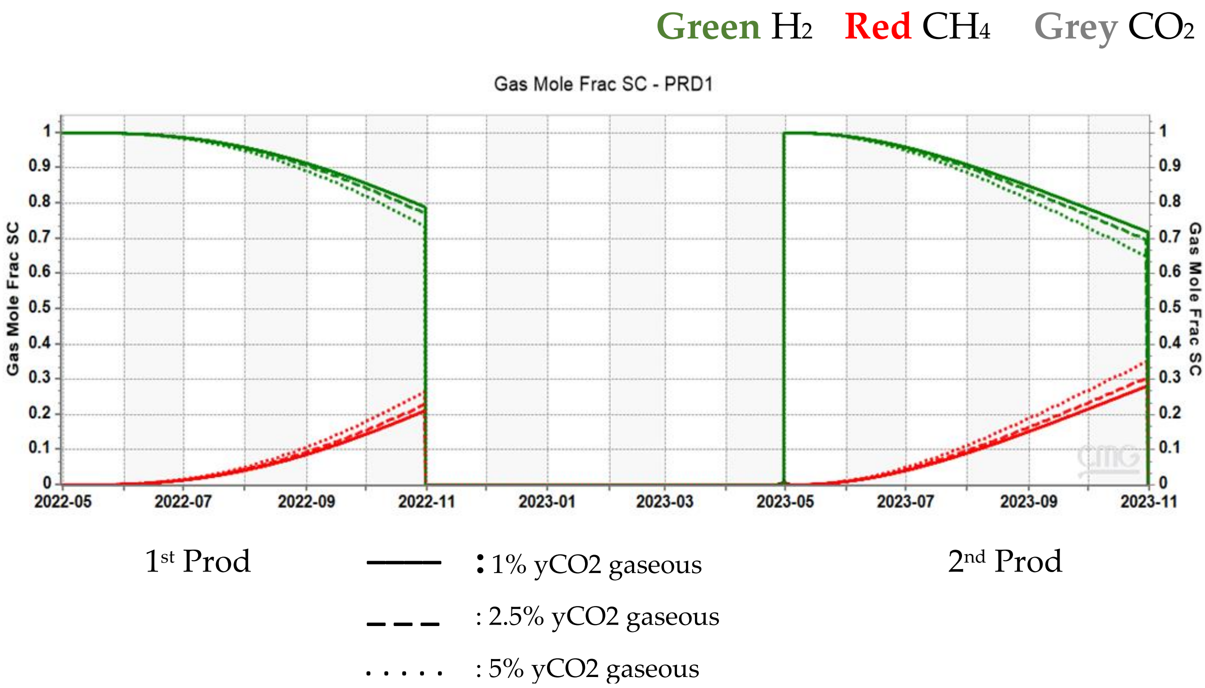


Figure 4-9: Gas Production Rate Composition – Different initial amount of Carbon Dioxide

Figure 4-9 shows how the Gas Production composition is influenced by the parameter and it could be seen that an increase in the bacterial losses is expected when the initial CO_2 amount is increased. This is because CO_2 is actually the limiting reactant; so with a greater amount of CO_2 available, methanogens proliferation can perpetrate more.

By looking at Figure 4-10 it is worth to notice that the overall Methanogenic Archaea loss is never surpassing the 3% value even when the depleted gas field CO_2 initial amount is up to 5%.

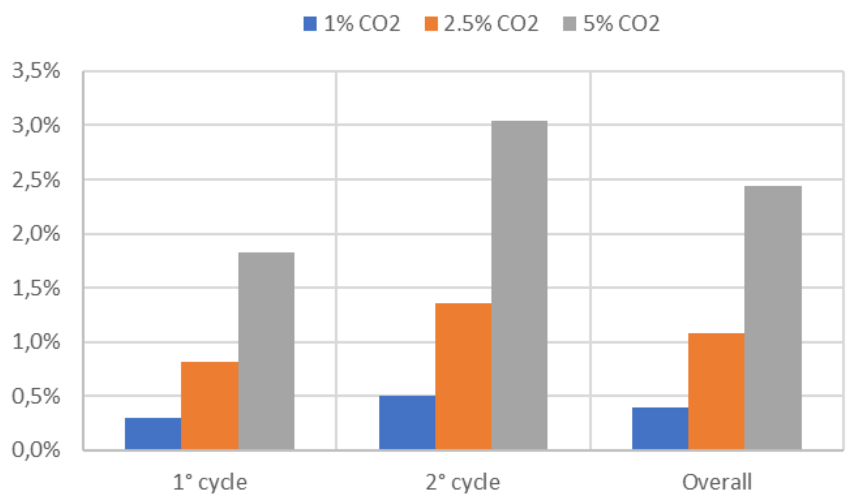


Figure 4-10: Losses due to Methanogens Proliferation

5 Realistic Energy Scenarios and Applications for UHS

5.1. General Introduction

The objective of this section is to simulate a realistic H_2 storage operation scenario over a decade in a depleted gas field. For this purpose ECHELON simulator was used. As described in the previous sections, ECHELON is a GPU-based reservoir simulator, that allows to achieve much higher computational performance with respect to CPU reservoir simulators such as STARS. This is why it is the preferred choice to tackle daily engineering simulations in real fields. This allowed to simulate the whole reservoir level of interest for the desired time span of ten years in an affordable simulation runtime.

ECHELON is currently not capable of accounting for chemical reactions, so bacterial growth was not included in this study. However, it was already proved, based on the results shown in Chapter 4, that hydrogen losses due to microorganisms are limited in cases like the one we are considering, where CO_2 concentration is low and can be neglected. Thus the main focus of this analysis is:

- the different cushion gas composition and amount and the effect on the gas production stream purity
- the aquifer impact on the production and pressure
- the number of storage wells and the storage Capacity in GWh_{LHV_H2}
- the different operation schedules and their impact on final results

Starting from an ECHELON model for the layer of interest, capable of adequately reproduce historical data and pressure trends for the field, whose production started in the 1970s, different set up for different storage scenarios were assumed using as a starting date 2023. The main inputs needed for the simulations could be reduced to Wells Definition and Schedule Definition (Surface Flowrate required for a specific period of time) more specifically they were:

- Injection stream composition (H_2 and CH_4),
- Location of the storage wells (for simplicity the same location for injection and production was assumed)
- Well operating controls: Injected/Produced Surface Flowrate
- Well operating limits: bottom hole pressure, water gas ratio
- Relative Permeabilities calculated using the saturation tables already present from the history data,
- Transmissibility coefficient which could be either directly inserted or calculated internally by the simulator using items already specified in the model generation that was done years ago: this last option was chosen,
- Well Bore Diameter [m] that is used both to calculate the transmissibility coefficient, the productivity/injectivity index and the effects of a D-factor
- Effective Kh (permeability * thickness) is calculated from the grid block data already present from the historic studies and this quantity also contributes to calculate the transmissibility coefficient
- D-factor for handling the effects of non-Darcy flow of free gas
- Pressure - equivalent radius r_0 which was calculated from the Peaceman's formula:

$$r_o = 0.28\frac{\left[D_x^2\left(\frac{K_y}{K_x}\right)^{1/2} + D_y^2\left(\frac{K_x}{K_y}\right)^{1/2}\right]^{1/2}}{\left(\frac{K_y}{K_x}\right)^{1/4} + \left(\frac{K_x}{K_y}\right)^{1/4}} \quad (5.1)$$

Dx, Dy: grid block dimensions
Kx, Ky: relative permeabilities in x and y directions

Well limits are reported in in Table 5-1 . As a starting point a storage cycle of 6 months injection followed by 6 months of production was assumed for the 10 years of the simulation. This configuration was used as a reference case for various sensitivities related to cushion gas and number of wells and to assess a reasonable storage working capacity.

Table 5-1: External Constrains

External Constrains	
BHP_MAX	360 bar
BHP_min	90 bar
WG-Ratio Max	1.00E-04
Max Flowrate	2% of Capacity

After that a more realistic schedule was implemented based on the Italian prospected hydrogen production, transportation and demand. To do that, from a detailed systematic energy analysis of Italy, a typical SoC yearly variation for UHS plants was derived, more details on the procedure will be found in Section 5.6 of this Chapter. From these data new Schedule Definitions were obtained with a Monthly and Daily variation. The resulting cases will be discussed in the next sections of this chapter.

5.2. Base Case Definition & Analysis

Similarly to the previous case study the cushion gas molecule for the base case was chosen to be hydrogen itself in order to get the maximum purity in the gas production stream. Few other parameters had to be decided: the number of wells, operational rates and cushion gas amount of the reference case that would allow to satisfy the operational constraints while maximising the storage capacity; these parameters were evaluated via preliminary sensitivity analysis. The final configuration for the base case was:

- Number of Wells: 5
- Rate per Well: 250.000 Sm^3/d
- Cushion Gas: H_2 injected for 3 months

This resulted in an available capacity for the reservoir equal to 2.2364E08 Sm^3 of H_2 injected in the 6 months period every year which can be converted to the energetic value of 633.7 GWh_{LHVH2} using the LHV of H_2.

Notably, the Energy Production of the various production periods of each year varied during the decade of operation and was always greater than the 633.7 GWh_{LHVH2} expected as reported in Figure 5-1

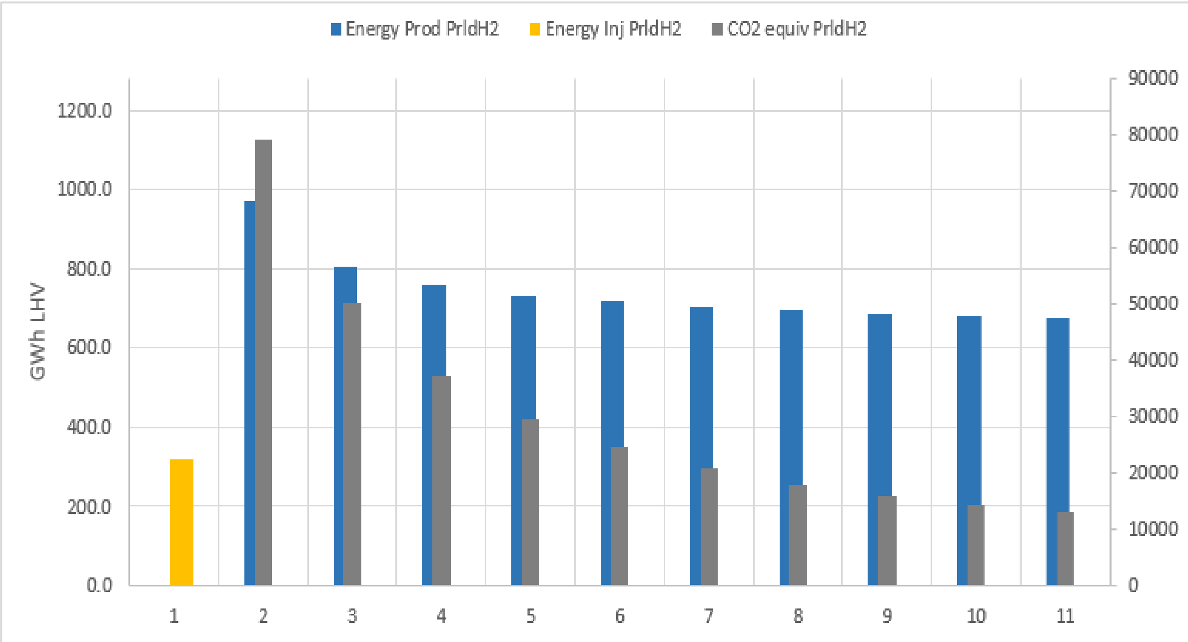


Figure 5-1: Energy Production and CO_2 equivalent emissions

The main reason is that even if H_2 is used as cushion gas, methane is still present in the reservoir. This means that the mixing process between the molecules will occur as showed by the H_2 molar fraction trend represented in Figure 5-2. Thus, since some methane reaches the surface instead of hydrogen the global energy content of the production stream is going to be grater being the LHV [MJ/Sm^3] of methane higher than the one of hydrogen. Nevertheless, since only hydrogen is injected in the various cycles, this effect is strongly dumped over the timeframe of operation and the purity of the stream increases over time.

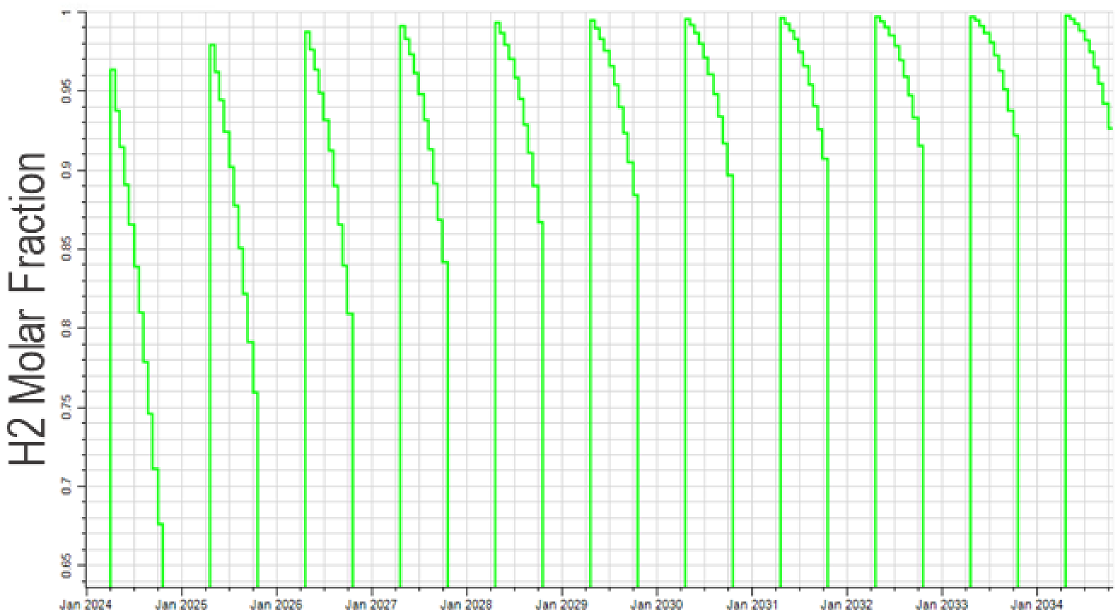


Figure 5-2: Molar Fraction trend

Together with the Energy Production content Figure 5-1 also shows the amount of equivalent CO_2 emitted [tons] by using the production stream in any industrial application (being combustion the most common). The value was calculated from the amount of CH_4 moles in the production stream considering its total conversion to CO_2 and then, from the molar amount using the molecular weight the tons value was obtained. As the methane amount in the production stream decreases over the years of operation also the equivalent CO_2 amount emitted follows the same trend.

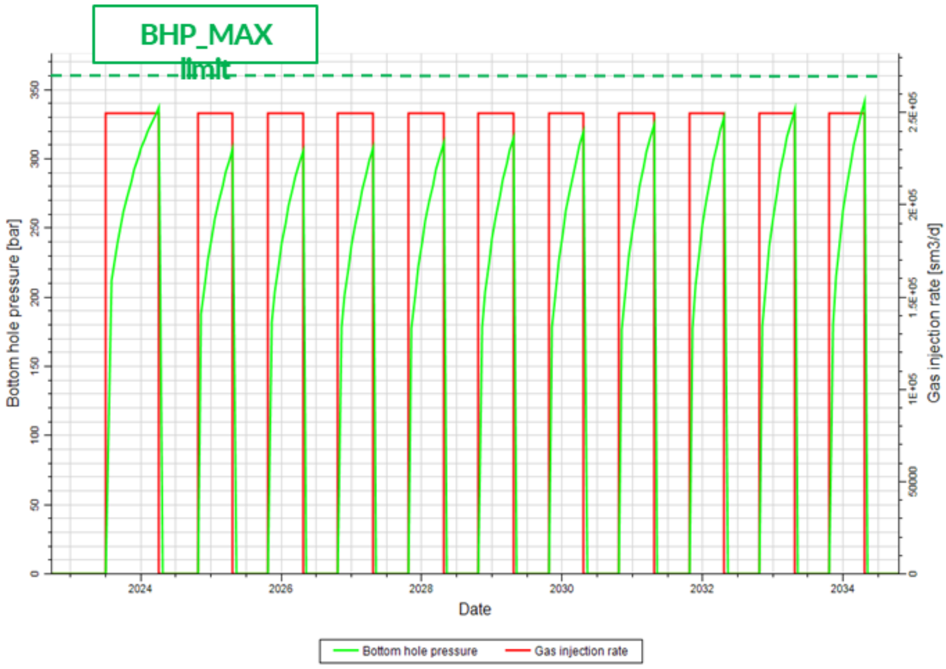


Figure 5-3: Injection schedule for Base Case

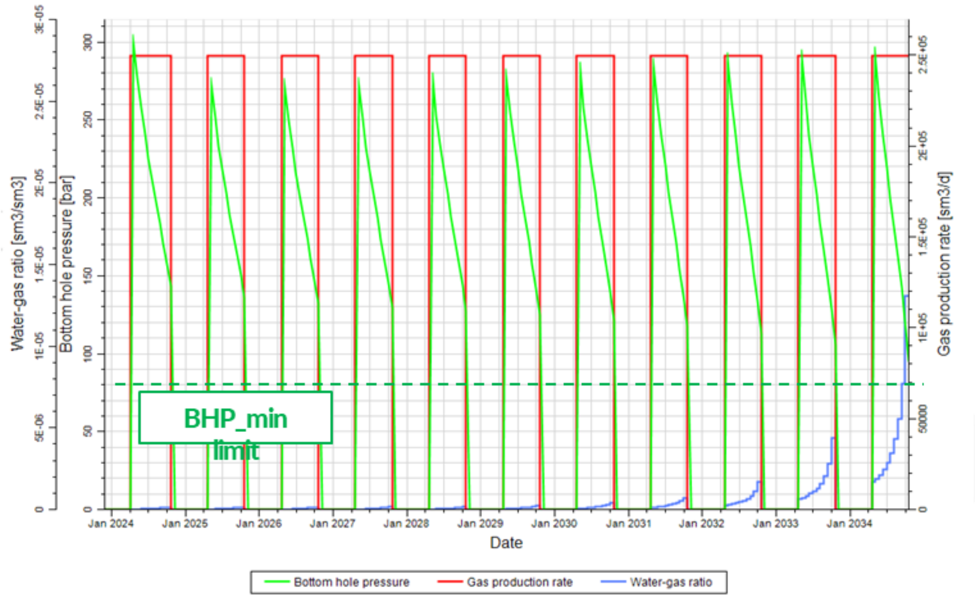


Figure 5-4: Production schedule for Base Case

Figure 5-3, for the injection phases, and Figure 5-4, for the production phases, show the response of a representative well. Similar conditions were observed for all other wells and are not reported for brevity. This consideration remains true also for the subsequent cases.

Since this is the Base Case, no limitations were reached, meaning that the wells could operate in the expected conditions and that the parameter described above in this section were correctly evaluated.

5.3. Methane as Cushion Gas

Once again the possibility of using methane as cushion gas is analysed.

From the previous case study a decrease in production stream purity was expected, this statement demonstrated to be true but only for the first few years of operation as it could be seen from the Figure 5-5 that shows the different molar concentration of hydrogen of this case with respect to the Base Case.

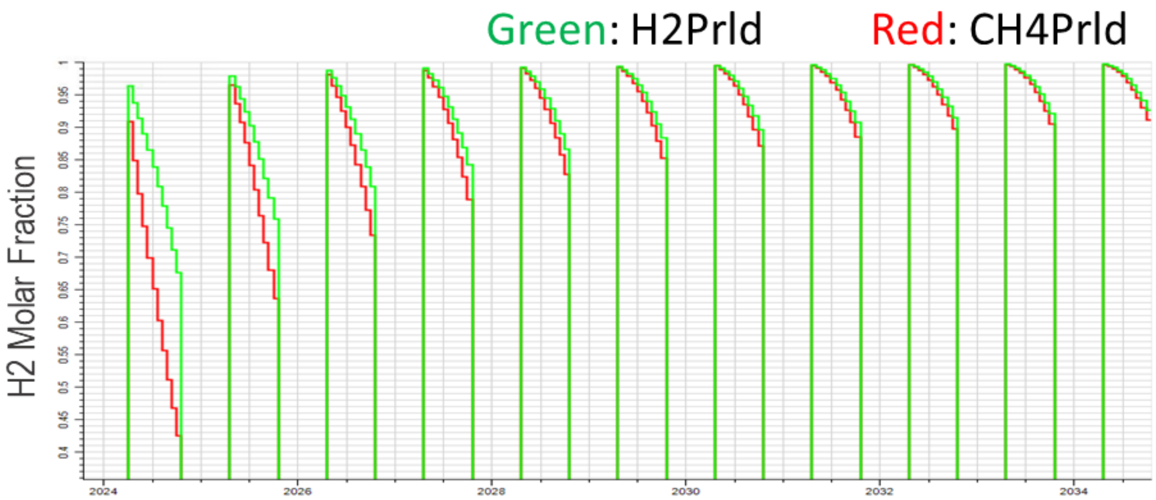


Figure 5-5: Molar Fraction trend

The energetic analysis reported in Figure 5-6 shows some peculiarities of this case compared to the Base Case already analysed.

First, as expected, the energy injected in the form of cushion gas in this case is much higher: this can be seen both as disadvantage by the energetic point of view and as an advantage from an economic standpoint since methane is actually much cheaper than hydrogen up to date. Anyway, predictions on realistic prize of hydrogen in future years are quite wide in range and an advanced economic evaluation deems out from the scope of this thesis.

Next, it is important to point out the strong gap between the equivalent CO_2 emitted in the first years between the two cases. As expected by the previous analysis this is the time-span in which methane present in the reservoir can mix with the injected hydrogen and is then reproduced together with it by the production wells. These results show that the impact of the cushion gas molecule is quite relevant for the first years and should be taken into account when deciding the cushion gas composition in order to not excessively compromise the purity of production stream of the first years of operation.

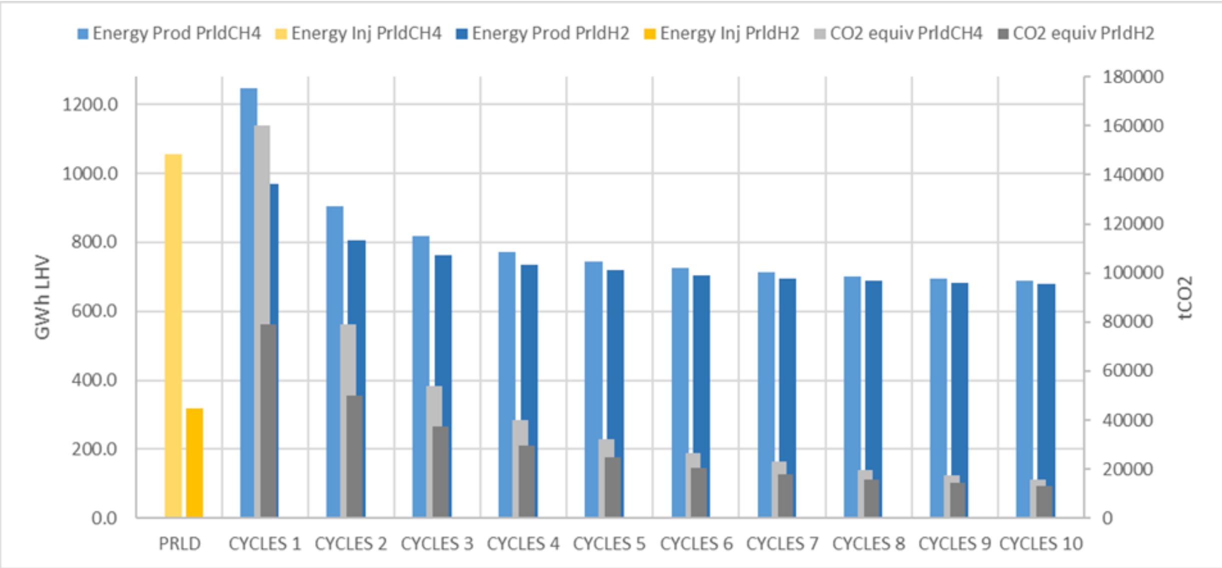


Figure 5-6: Energy Production and CO_2 equivalent emissions

At last is should be mentioned that methane has bit higher compressibility factor at pressure and temperature conditions reported in the reservoir, hence the reservoir pressure is going to be a bit smaller in this case with respect to the Base Case as it can be seen in Figure 5-7. The effect is dumped and the two curves tend to overlap later in time.

Green: Base Case   Red: Methane as cushion gas

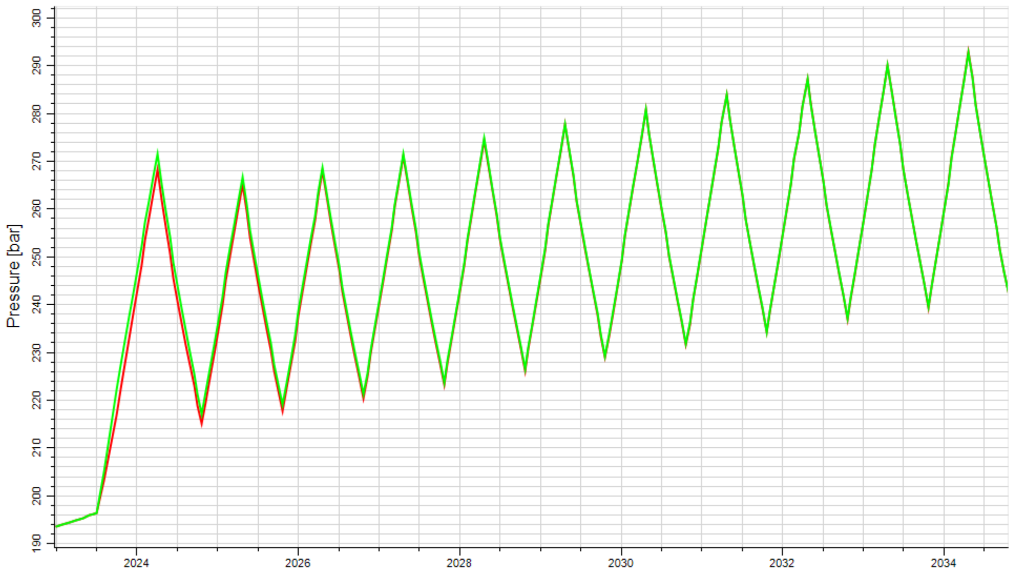


Figure 5-7: Pressure evolution during H_2 storage operations

5.4. Different amount of Cushion Gas injected

Here a sensitivity analysis on the different amount of cushion gas injected is carried out. The molecule chosen for all the cases is H_2 as in the reference case. As it was stated before the Cushion Gas injected represents an economic upfront investment, so the objective is to try to minimize it, without compromising the stability and long term performance of the storage. Two different scenarios are analysed here: one in which the amount is halved and the other one in which is doubled with respect to the Base Case.

5.4.1. Reduced Cushion Gas injected

In this case the energy lost in cushion gas is reduced from 318.8 GWh_{LHVH2} of the base case down to 159.4 GWh_{LHVH2}. As expected, reservoir pressure will oscillate on lower values as reported in Figure 5-8 even if the values are still acceptable considering the constrains imposed previously in Table 5-1.

Green: Base Case Red: Halved cushion gas

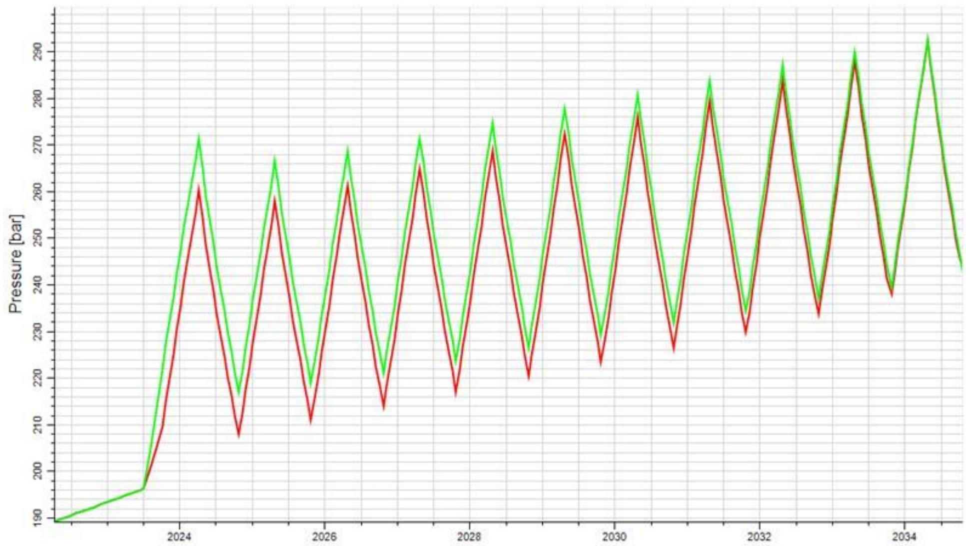


Figure 5-8: Pressure evolution during H_2 storage operations

The same can be said on the injection response of the wells showed in Figure 5-9; this because problems during injection arise when the pressure in the reservoir is high and that is not the case.

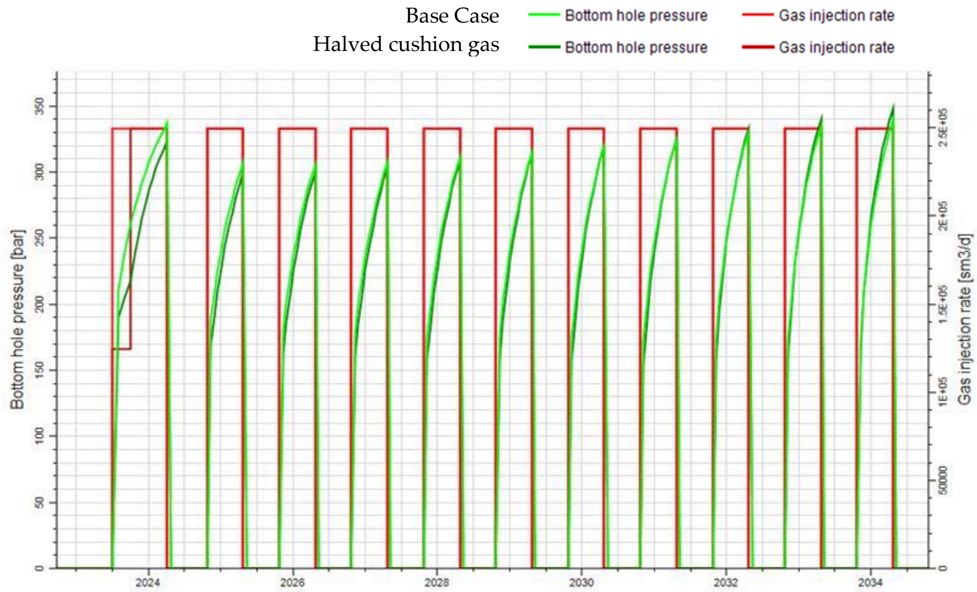


Figure 5-9: Injection schedule for Halved cushion gas amount

However, the opposite can be seen when the wells are operated as producers, where a low reservoir pressure favours the reaching of minimum Bottom Hole Pressure at which wells can operate. When this limit is reached the scheduled flowrate can't be honoured and starts to decrease as it can be seen in Figure 5-10.

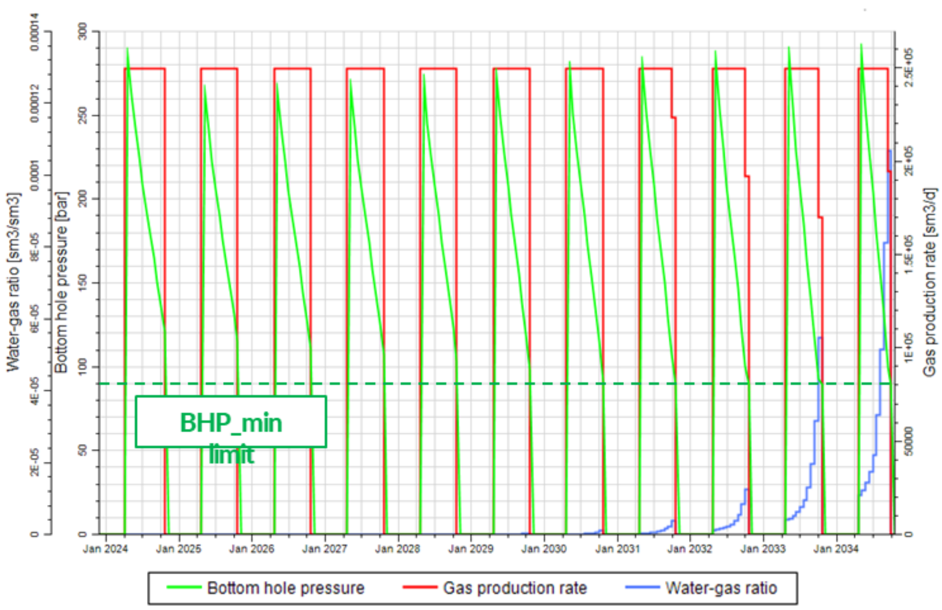


Figure 5-10: Production schedule for Halved cushion gas amount

5.4.2. Increased Cushion Gas injected

Here the energy lost in cushion gas is increased from 318.8 GWh_{LHVH2} of the base case up to 637.6 GWh_{LHVH2}. Differently from the previous case the reservoir pressure will now oscillate on higher values as reported by Figure 5-11.

Green: Base Case Red: Doubled Cushion Gas

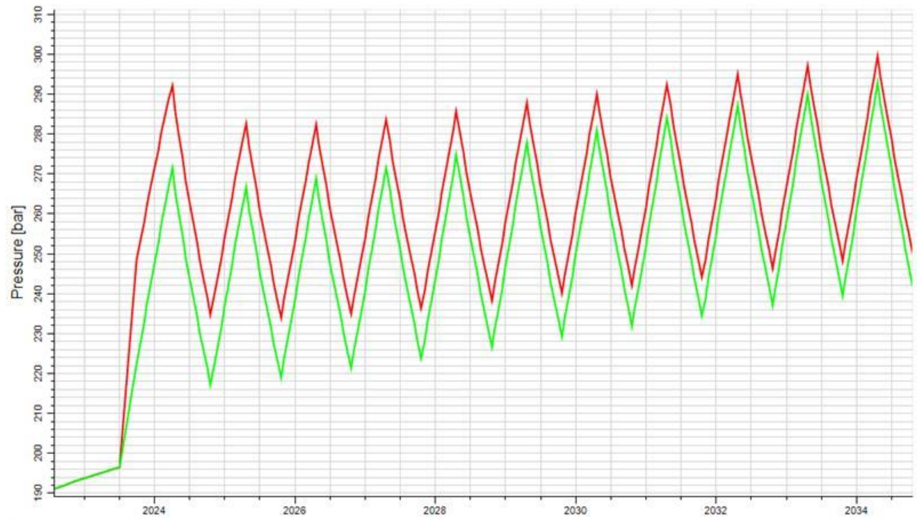


Figure 5-11: Pressure evolution during H_2 storage operations

As it can be imagined this may represent a problem for the injection phases: Figure 5-12 shows that the issue arise only during the first injection cycle which happens immediately after the preload injection, hence when the gas inventory in the reservoir is at its maximum. This problem could possibly be mitigated if an idle period is inserted in the schedule, but further analysis should be done on these aspects in future development projects.

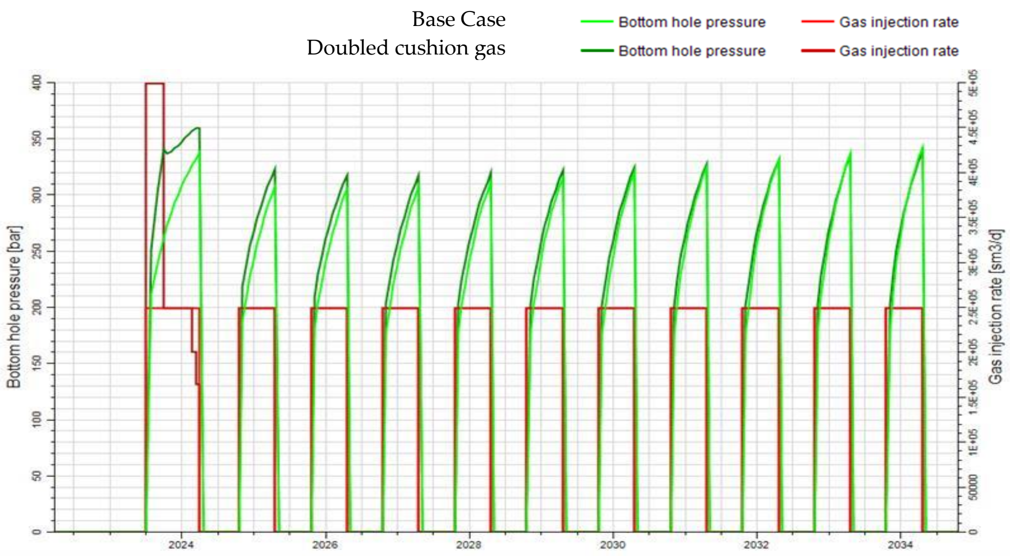


Figure 5-12: Injection schedule for Doubled cushion gas amount

Figure 5-13 shows the benefits that the production phases will have if this amount of cushion gas injection is chosen. First of all, with respect to the previous case no problems on minimum Bottom Hole Pressure arise, then with respect to the Base Case it can be seen that in the last years the water gas ratios is lower. This data suggests that thanks to a higher average reservoir pressure during the H_2 storage operation period the aquifer influx was mitigated and its impact minimized.

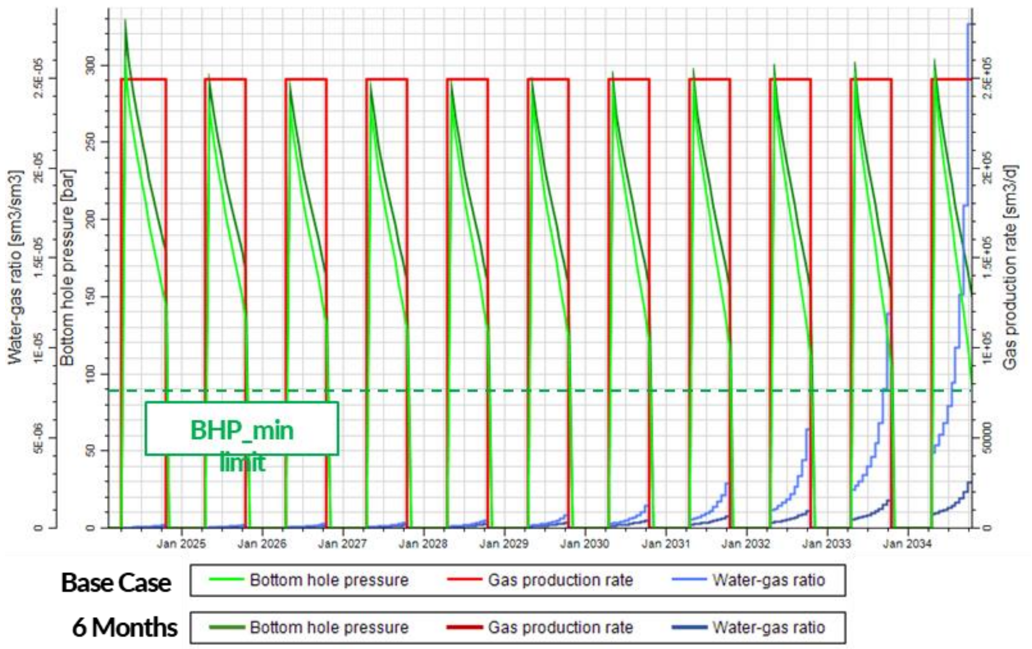


Figure 5-13: Production schedule for Halved cushion gas amount

The last aspect that was highlighted by the different amount of cushion gas injected was the purity variation: especially in the first cycles. As showed in Figure 5-14, in the first years of operation the gas production stream of this last case will be much better with respect to the Base Case and the halved injected cushion gas case. The impact will decrease as the operation time goes on.

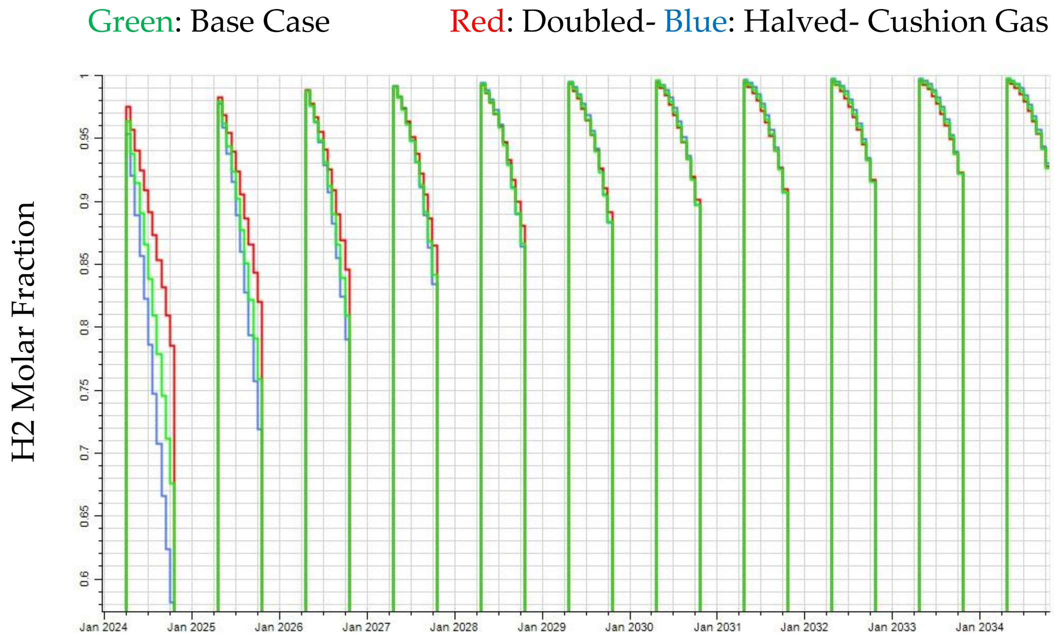


Figure 5-14: Molar Fraction trend

5.5. Different Number of Wells in operation

Once the discussion over the cushion gas was done both on the molecule and on the amount to be injected, a sensitivity analysis on the number of wells was performed in order to evaluate the effective Capacity available for the depleted gas field level L3. Particularly two cases were simulated one increasing the number of wells up to 7 and the other one getting up to 10, which means doubling the value of the initial Base Case. For all the cases the cushion gas is kept constant so that the initial pressure in the reservoir is the same.

5.5.1. Seven operating wells case

With seven operating wells at the same flowrate per well (equal to 250.000 Sm^3/d) the total ideal Energy Capacity would increase from 633.7 GWh_{LHVH2} up to 887.2 GWh_{LHVH2}. This improvement has to be reached without violating the constrains reported in Table 5-1. Figure 5-15 shows how increasing the total flowrate will increase the global variation in reservoir pressure per cycle.

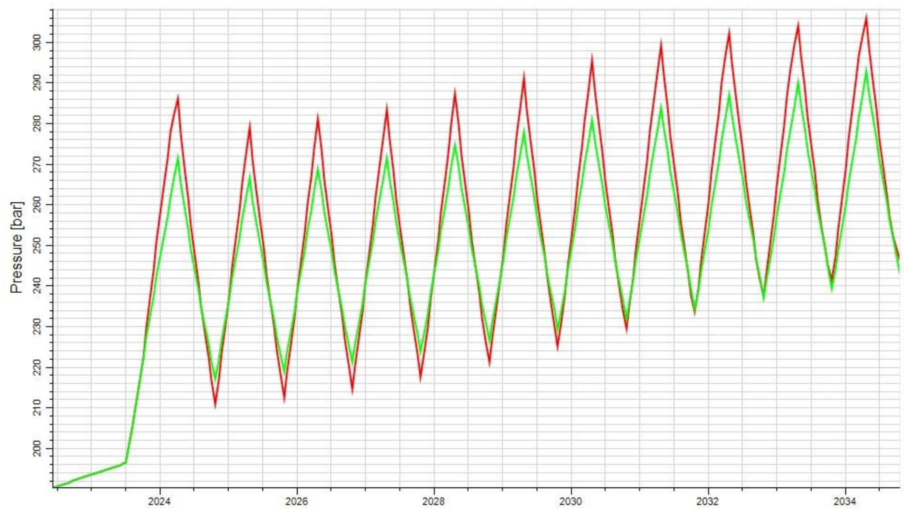
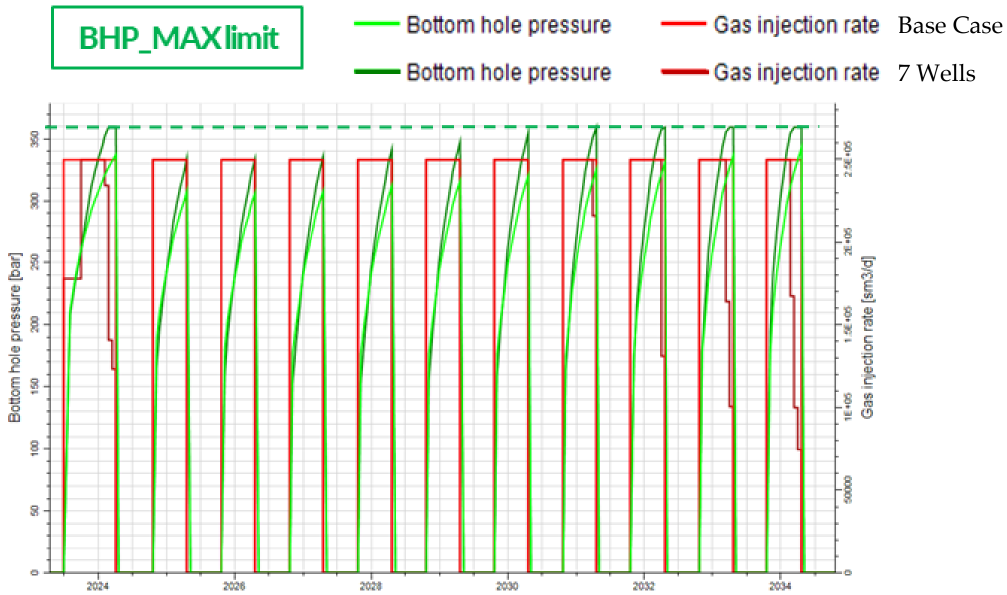


Figure 5-15: Pressure evolution during H_2 storage operations

Looking at the injection phases (Figure 5-16) once again the main issue is the reaching the maximum Bottom Hole Pressure, as it was already seen in Section 5.4.2, at the first injection cycle immediately after the cushion gas injection. Even if this problem may be tackled with the consideration of an idle period the same issue comes up during the last years of operation making this alternative less feasible.

Figure 5-16: Injection schedule for 7 Wells in operation



The situation gets even worst when analysing the production phases: in fact, for the first six years of operation no limitation is violated even if the variation of pressure per cycle is strongly increased due to the higher flowrate processed.

However, in the last years the minimum pressure becomes too low and violates the Bottom Hole Pressure limit (Figure 5-17), furthermore the water-gas ratio is strongly increased meaning that the pressure in the reservoir is getting too small for long periods of time and the aquifer rise brings some water up to the production wells. It is worth to emphasize that producing water is a critical effect that have to be avoided, this is why a techno-economic limit on the maximum water-gas ratio was considered.

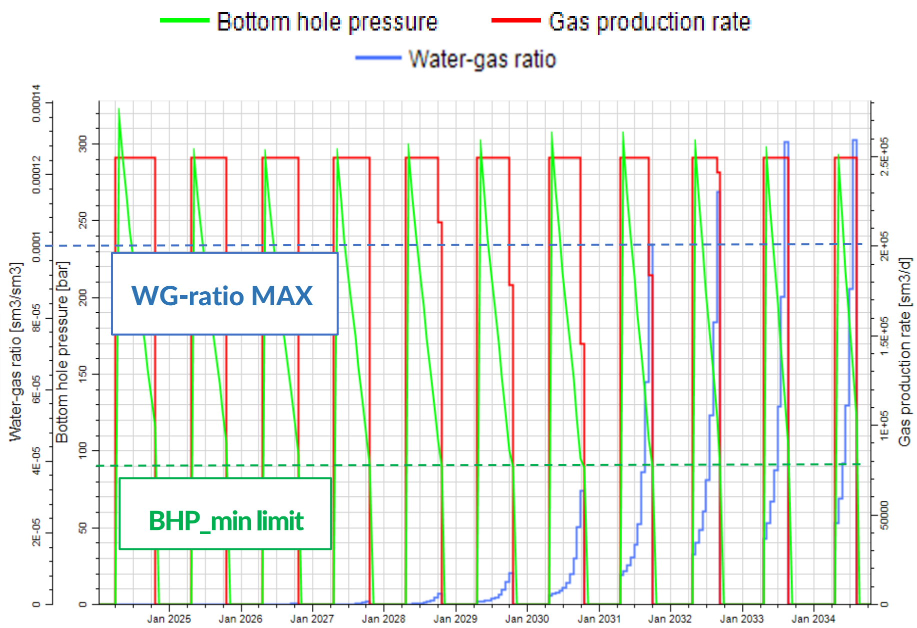


Figure 5-17: Production schedule for 7 Wells in operation

5.5.2. Ten operating wells case

With ten operating wells the total ideal Energy Capacity would be doubled with respect to the Base Case and reach 1267.4 GWh_{LHVH2}. Once again, this improvement would be possible only if constrains presented in Table 5-1 would not be violated.

Same issues as highlighted in the 7 wells case may be observed. It is important though to understand the reason behind this behaviour and which parameter can be modified to get an higher storage capacity for this depleted gas field level. This is why the behaviour of the production wells reported in Figure 5-18 is particularly important. Here it is showed without doubt that when a too low pressure is required at the bottom wells the water coming from the aquifer is going to be sucked up to rebalance the pressure value and already after the fifth year of operation for some time the well is stopped due to the reaching of the maximum water gas ratio limit. This condition was not reached in the seven wells operation scenario and suggested that long period at low pressure should be avoided during the schedule definition.

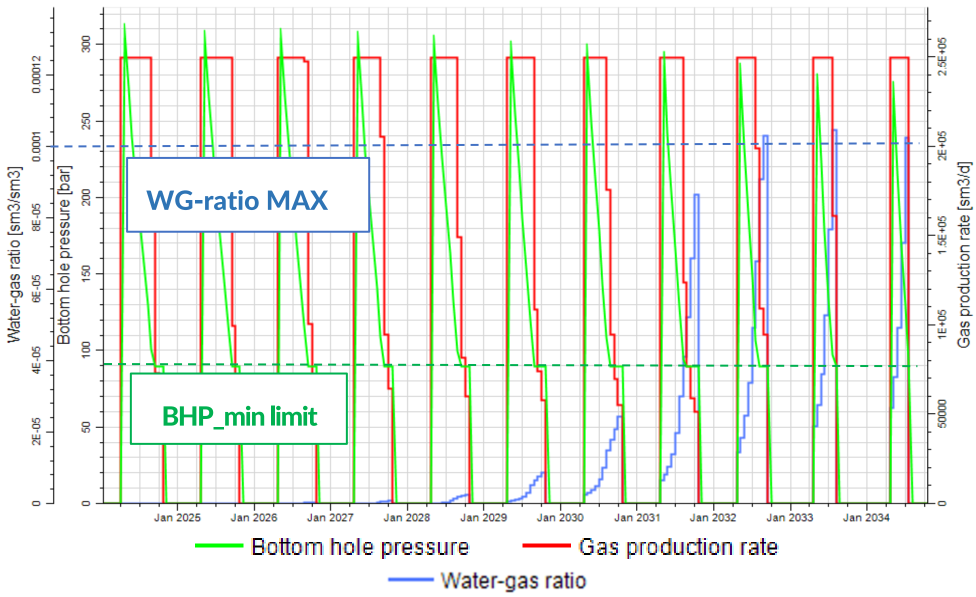


Figure 5-18: Production schedule for 10 Wells in operation

5.6. Realistic storage operation scenarios

After a characterization of the depleted gas field level made using standardized 6 months constant injection and 6 months constant production cycles, more realistic scenarios wanted to be considered. Particularly by increasing the flexibility on the flowrate variation scheduled getting down to monthly based and daily based cycles to capture the actual requirement of hydrogen injection and production that might occur in realistic projection of hydrogen developed economy and infrastructure.

These data were found in the study [29] on an Italian decarbonised energy system scenario description considering different investments and development on:

- Renewable production energy plants,
- Innovative plants to produce sustainable fuels and reduce fossil fuels demand,
- Improvement in transportation grids of different energy vector: electricity, hydrogen, CH_4-H_2 blend, liquid fuels
- Improvement in storage systems global capacity and activation of new storage technology like the one of UHS described partially in this thesis

Since the national territory has numerous grid constrains for transporting different vectors a nodal representation with a regional resolution was adopted. A typical schematic representation of one node is shown in Figure 5-19 where all the different energy vectors and CO_2 flows are interconnected.

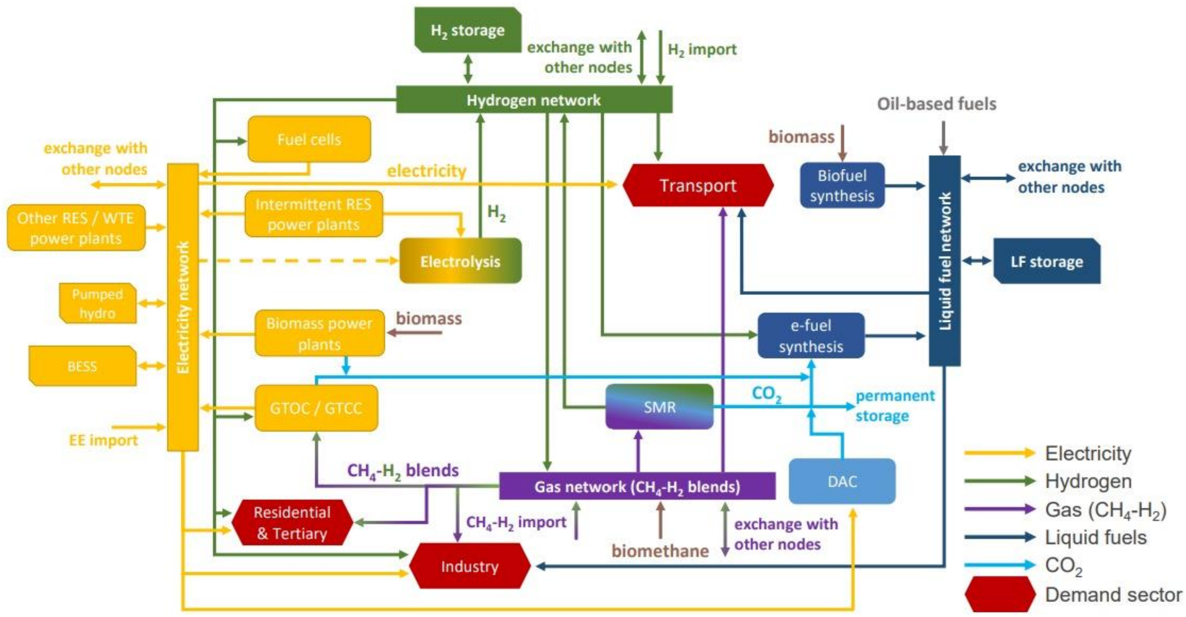


Figure 5-19: Schematic representation of the energy vector and CO_2 flows within one node

To be able to capture all the different effects of this interconnections a specific optimisation model was developed: the OMNI-ES model (Optimisation Model for Network-Integrated Energy Systems) [29]. This model was created by the research group of the Energy Department of Politecnico di Milano to support the activity of the Hydrogen Joint Research Platform [30]. This Platform objective is to evaluate the role of hydrogen in the evolution of the Italian energy system and the way in which hydrogen storage systems contribute to the balance between hydrogen production and demand and to the interchange of this energy carrier among the various Italian regions. This means that the model is able to investigate the cost-optimal solution under specific Net-Zero CO_2 emissions constrain. In input it requires different technical data and upper boundaries constrains on each specific resource availability in order to not overestimate the impact of any technology. Furthermore geo-localization of specific resource availability is crucial to determine the model final output since the transmission grids for the different energy vectors have to be optimized too. This means that optimum configurations are susceptible to changes if new data on resource availability are found. For example, if the depleted field analysed in this thesis is actually converted into a H_2 storage plant its position and its capacity should be added to the input data and the model would be able to find a different optimal solution with respect to the previous one.

Looking at the outputs, the model is able to give the total installed amount of each resource considered, plus for the energy storage plants, of which the UHS plants are part of, a non-dimensional State of Charge of a generic facility is given. The State of

Charge of a depleted gas field coming from this work is presented here in Figure 5-20 and was used as a starting point to create the realistic schedules cited above.

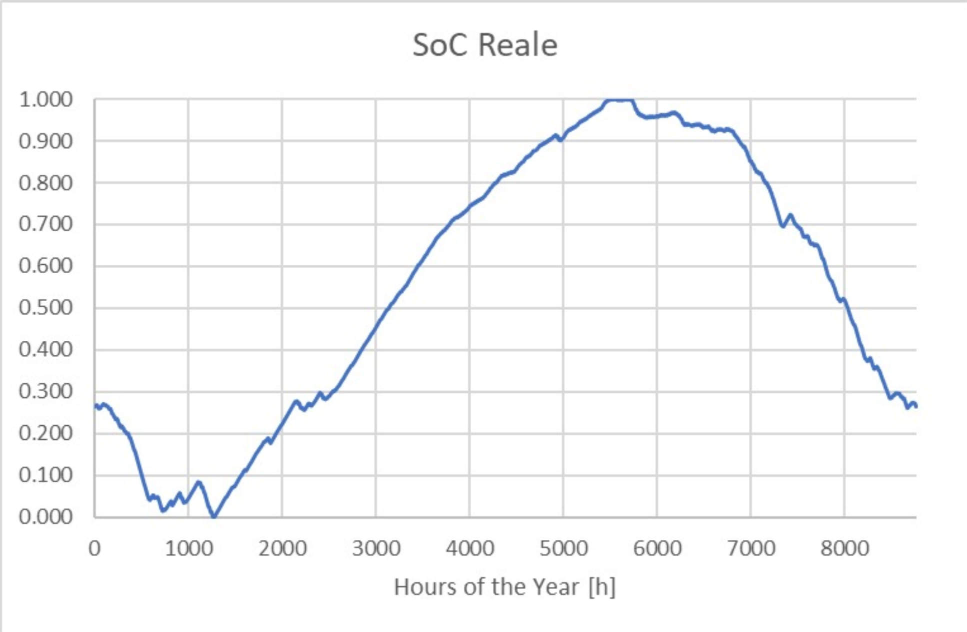


Figure 5-20: State of Charge projection for a UHS facility

In order to get the final Schedule to be inserted in ECHELON from the SoC graphic the following equation was used:

$$Q = \frac{dSoC(t)}{dt} * Q_{tot} \quad \text{with Q: flowrate [Sm}^3\text{/d] and Qtot: Total Capacity [Sm}^3\text{]} \qquad (5.2)$$

The derivative value was then discretized on different time-scales depending on the flexibility that had to be simulated (monthly/daily) while the total capacity inserted was equal to 2.2364E08 Sm^3 that corresponds to the 633.7 GWh_{LHVH2} evaluated in the previous section.

5.6.1. Monthly flexible Schedule

With a monthly averaged flowrate description the final Schedule is represented in Figure 5-21. It is possible to see that given the seasonal behaviour of the SoC graph the flowrate will be organized in 5 months of injection (Feb/yy – Mar/yy – Apr/yy – May/yy – Jun/yy) followed by 7 months of production (Jul/yy – Aug/yy – Sept/yy – Oct/yy – Nov/yy – Dec/yy – Jan/yy+1). The seasonal trend in hydrogen storage is not a given constrain but was actually a result of the OMNI-ES model, hence it can change if the input to the model are changed.

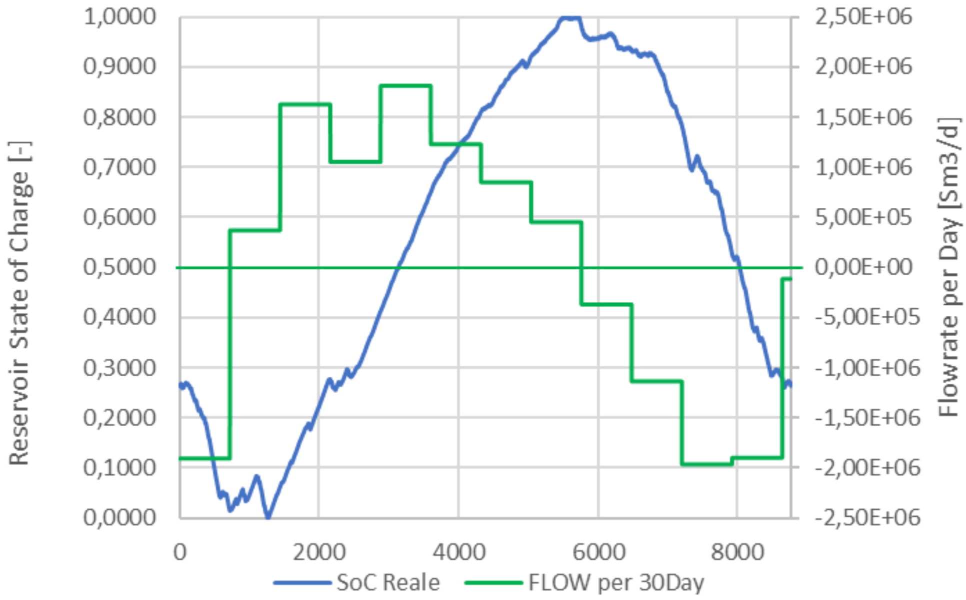


Figure 5-21: State of Charge and Scheduled flowrate projections for Monthly based case

Due to this unbalance between the different time available for the two phases much higher Gas Production Rate will be scheduled for the 5 months with respect to the constant value of the Base Case.

Similarly to what happened for the case in Section 5.5.2 the Bottom Hole Pressure limit was reached this time at the 8th year of operation and the production flowrate had to be lowered as reported in Figure 5-22.

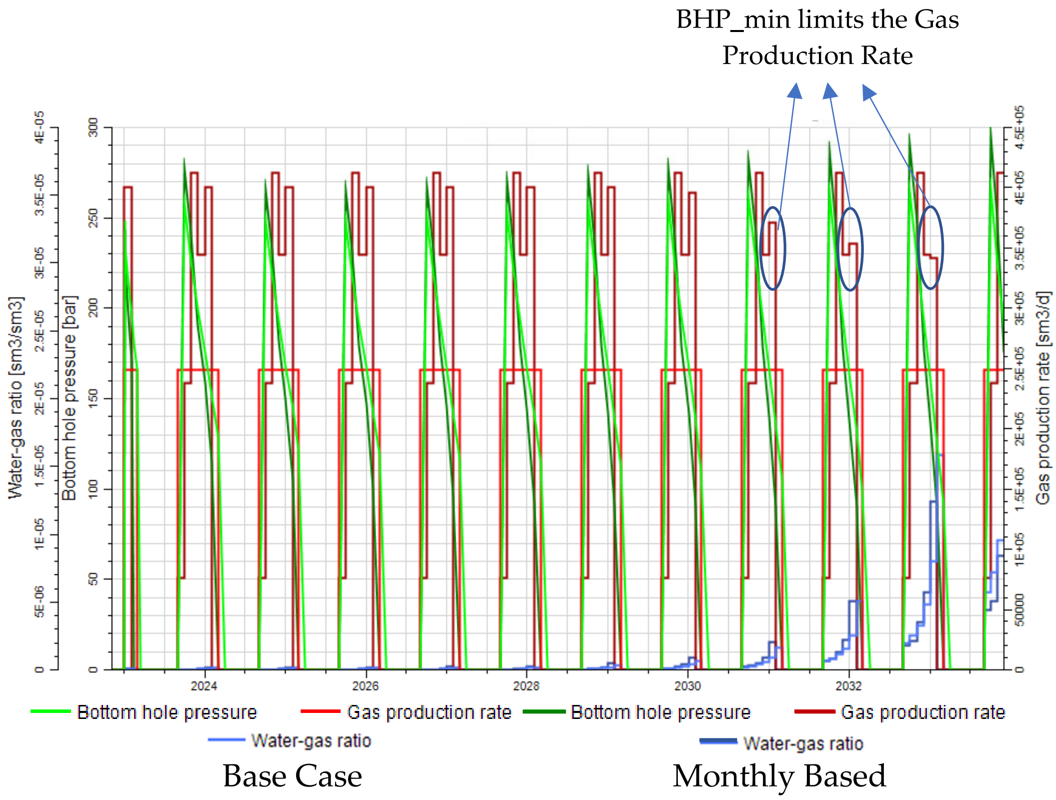


Figure 5-22 Production schedule for Monthly based Schedule

In the end no other particular change was highlighted with respect to the 6 months injection/production cycles operation meaning that the impact on the final operation results of a monthly schedule was limited.

5.6.2. Daily flexible Schedule

At last a Daily averaged schedule was used. This was the maximum flexibility that could realistically be implemented for a hydrogen storage plant since for similar plants designed to store natural gas this type of scheduling is doable.

Figure 5-23 shows the scheduled scenario and it can immediately be seen that with respect to previous cases there is not a clear difference between an injection and a production phase. Even if the overall seasonal trend is maintained the switching between production and injection operation occurs many times during a single year.

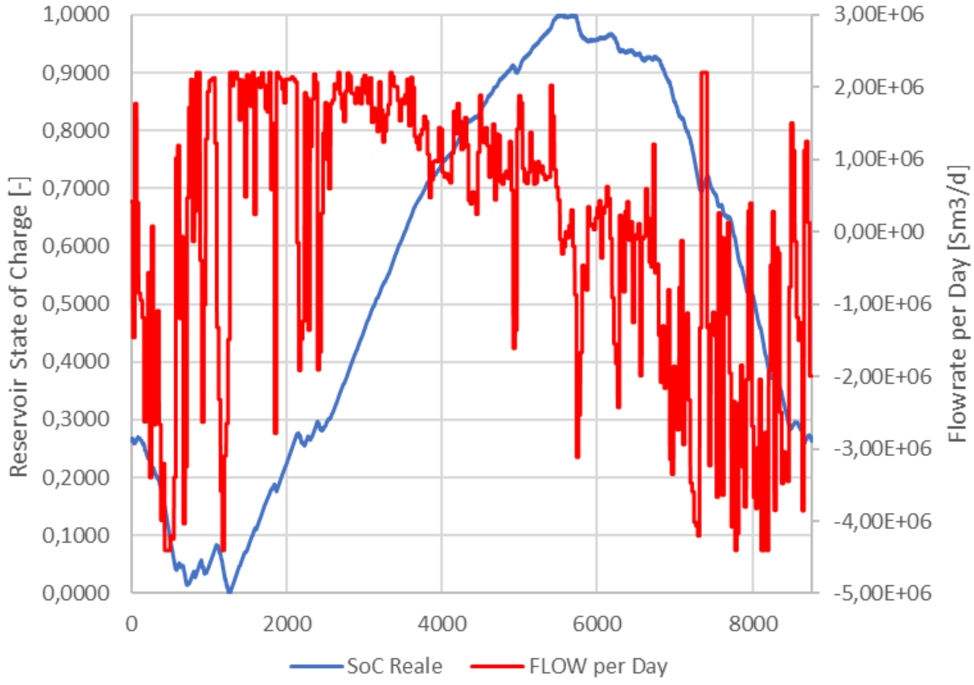
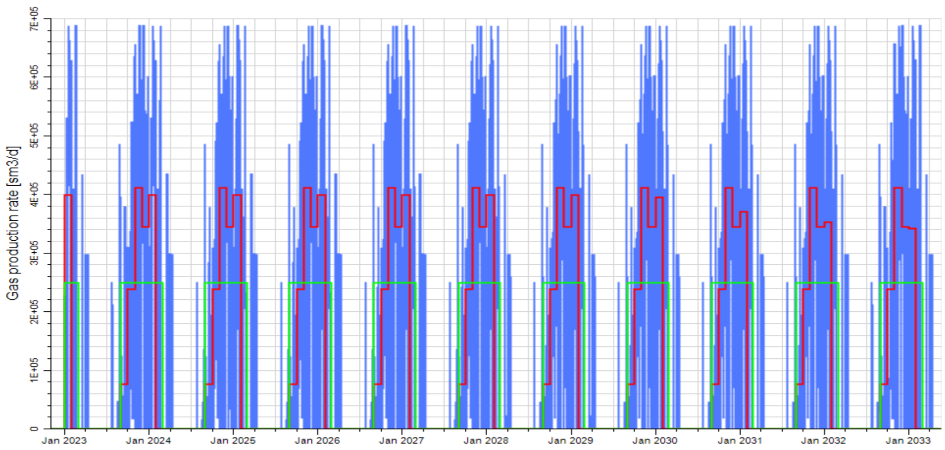


Figure 5-23: State of Charge and Scheduled flowrate projections for Daily based case

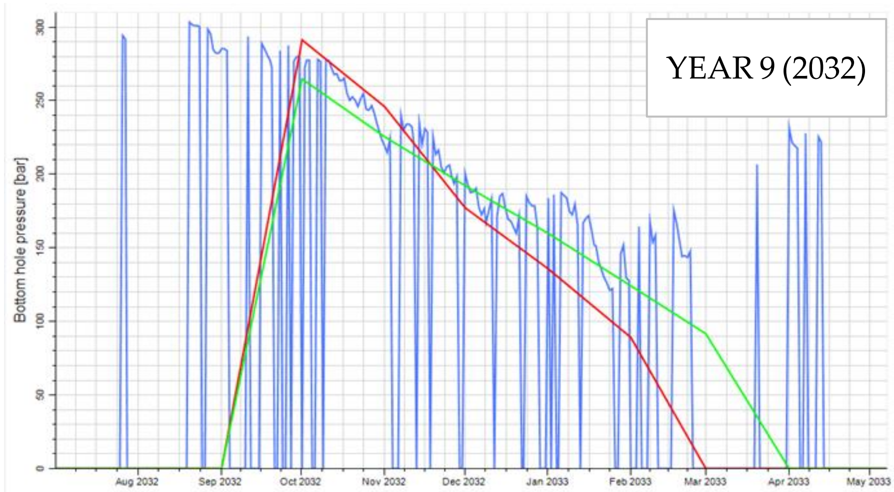
By looking at the Gas Production Rate schedule depicted in Figure 5-24 the increasing in the maximum value is even higher with respect to the monthly based scenario and reaches up to 1.5% of the Reservoir Capacity (kept constant at 633.7 GWh_{LHVH2}); this value is under the 2% limitation reported in Table 5-1 so the case was considered to be acceptable. Another important thing to notice is that the cycles perfectly repeat themselves year after year over the decade meaning that no limitation on Bottom Hole Pressure and Water-Gas ratio was reached. This was not the case for the monthly based scenario.



Blue: Daily Red: Monthly Green: 6 Months

Figure 5-24: Gas Production rate evolution during a decade of operation

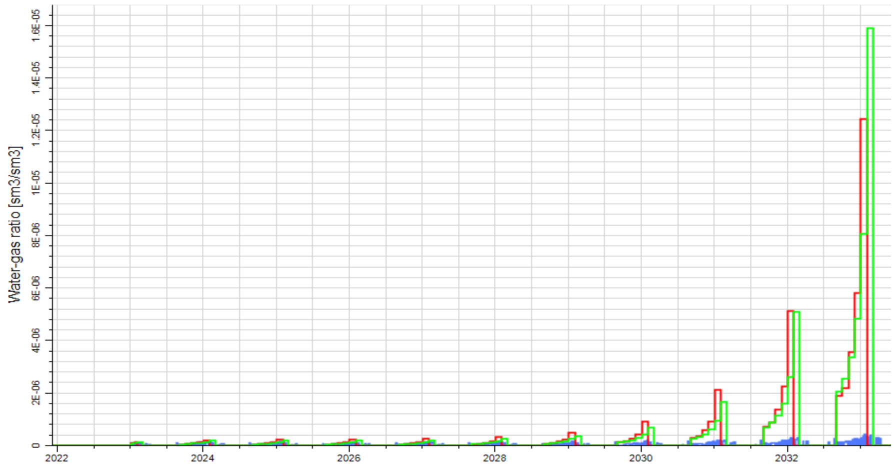
To get what is happening for this case a detail on the Bottom Hole pressure of the 9th year of operation is reported in Figure 5.25. Here it can be seen that the green and the red curve have a continuously decreasing trend with the red one ending a month early with respect to the green one since the monthly variable case has just 5 months of continuous production while the base case has 6 as previously stated. The daily based case instead has a production timeframe spread all over the year with an increase in April and May. Furthermore, frequent variations are observed and many times the value becomes equal to 0, meaning that the well has switched its operation to injection.



Blue: Daily Red: Monthly Green: 6 Months

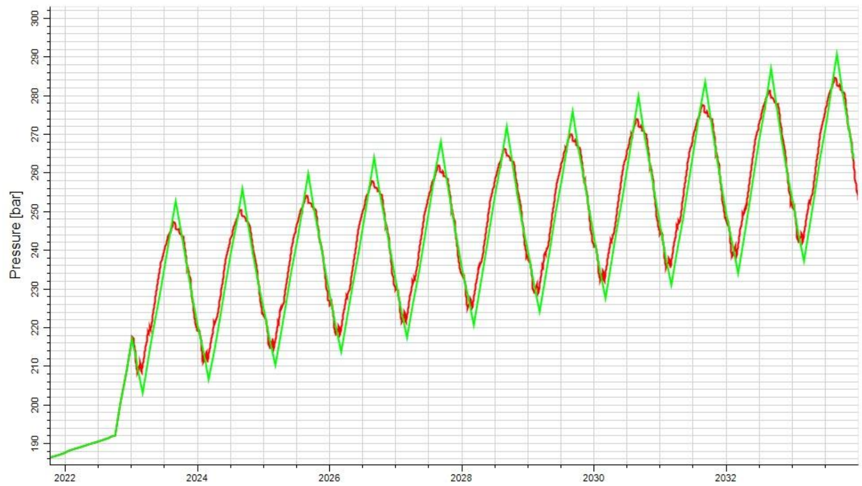
Figure 5-25: Bottom Hole pressure evolution of the 9th year of operation

Particularly this switching procedure was found to be very beneficial to the gas field as by comparing the water-gas ratio of the three different cases, see Figure 5-26, the one with daily flexibility remained low for all the decade while the other two increased especially in the last years. This happened because in the daily variable scenario the reservoir pressure oscillation over a single year was lowered with respect to the base case as reported by Figure 5-27. This means that the minimum pressure reached by the reservoir is higher and kept for less time, so the aquifer influx importance is lowered.



Blue: Daily   Red: Monthly   Green: 6 Months

Figure 5-26: Water Gas ratio evolution over a decade of operation



Red: Daily   Green: 6 Months

Figure 5-27: Pressure evolution during H_2 storage operations

The last relevant effect that was observed is the strong decrease, especially in the first years of operation, of the equivalent CO_2 amount emitted with respect to the Base Case. As already said, this value is directly correlated to the CH_4 concentration in the gas production stream. This means that the mixing phenomenon of hydrogen and methane happening in the subsurface formation is discouraged by a frequent injection and withdraw alternation. The reason is that hydrogen is going to have less time to disperse in the available porous volume interacting with the trapped methane already in place at the beginning of H_2 storage cyclic operation.

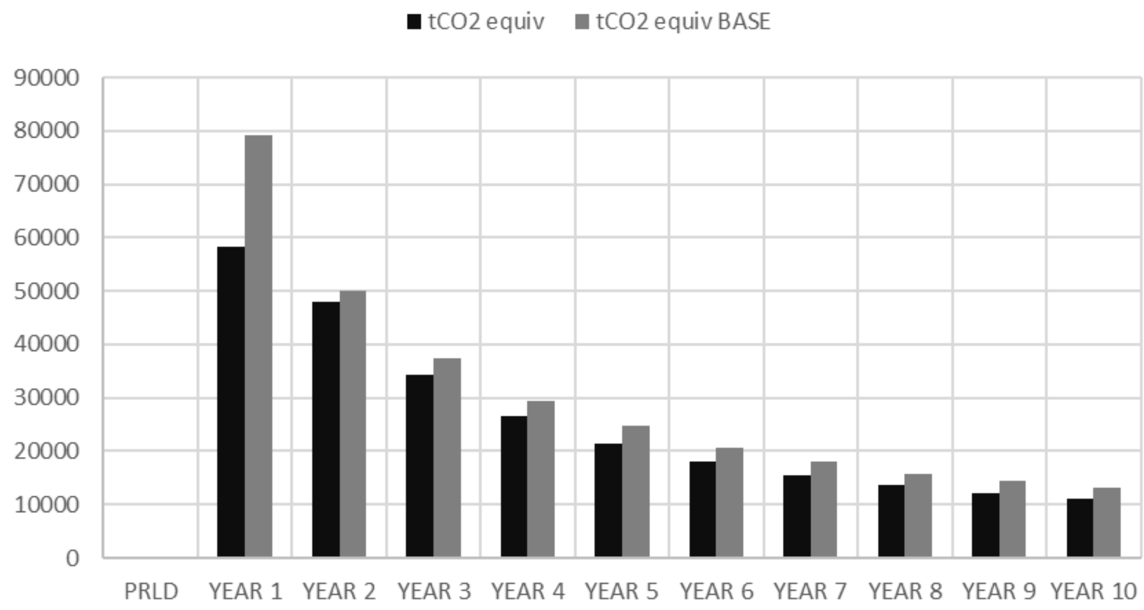


Figure 5-28: CO_2 equivalent tons emitted: Daily vs Base case

6 Conclusion and future developments

6.1. Underground Chemistry

From simulations on Methanogenic Archaea results showed that:

- Methanogens Proliferation occurs dramatically only if lot of carbon dioxide for the fixation mechanism is available, hence a proper estimation on the amount of CO_2 present in the initial gas field composition is crucial.
- The storage facility can't be used both as a H_2 storage plant and as a CO_2 sequestration plant, since the CO_2 injected to act as cushion gas will inevitably react with H_2 and enhance the archaea proliferation bringing the aqueous

concentration of methanogens archaea two order of magnitude higher than all other cases simulated.

- Methanogens Proliferation can be neglected if the initial CO_2 concentration is lower than 5%; furthermore, the by-product of the proliferation reaction is methane a molecule that would already be present in any case in the gas production stream and represents an energy source as well.

Future developments on this topic will include:

- The tuning of a Power-Law description for the sulphate-reduction bacteria for realistic storage facilities in order to evaluate the amount of H_2S that could pollute the gas production stream. This development should be coupled with a proper estimation on the amount of SO_4^{2-} present in the reservoir.
- Since these microbial reactions depend strongly on the $SO_4^{2-}$and CO_2 present in reservoir a coupling process of the bio-chemical model with the geo-chemical characterization of the reservoir site is required to better evaluate CO_2 presence which is influenced by CO_3^{-} carbonate and SO_4^{2-} evolution that are both strongly correlated to geochemistry
- Performing experimental activities aiming at characterizing the presence and activity of in situ microbial communities of the reservoir storage of interest, together with tuning of the main kinetic parameters for the bacterial growth to be adopted in the simulation cases.

6.2. Reservoir Storage Operability

Reservoir storage operability was analysed and the final conclusions are reported here:

- The choice between methane and hydrogen as a cushion gas molecule will mainly impact on the production stream purity of the first cycles of operation correlated to the amount of CO_2 equivalent emissions
- The amount of cushion gas injected should be evaluated specifically for each facility depending on the reservoir pressure and eventual aquifer influx. It was clear from the sensitivities performed, that a longer cushion gas injection will result in a better water management and if hydrogen is the molecule used, also a better purity in the gas production stream, even if the impact is once again restricted to the first years of operation.
- The choice of the number of wells together with their maximum operational gas flowrate is related to the Capacity [Sm^3] and the properties of the storage site.
- The frequency and alternation of charge/discharge cycles, considering realistic storage scenarios based on a future decarbonized energy system showed no meaningful variation for the monthly case while gave sensible benefits in the

daily case particularly on water management (WG-ratio last year: daily case 1E-08 versus 6 months case 1E-06) and production stream purity (CO_2 equivalent tons emitted in ten years of operation: daily case 258769 versus 6 months case 303160).

Future developments on this side are:

- Optimization of well location and the activation of group controls in order to maintain the target production/injection rates even if some of the wells may reach their physical limits.
- The evaluation of different cycle frequency for the realistic scenarios, i.e. weekly cycles, and different depleted gas reservoirs (which might present different petrophysical properties and aquifer strength)
- The testing of plant components to evaluate their readiness to flexible H_2 injection and withdraw
- Analyse different storage scenarios starting from the OMNI-ES model getting different flowrate schedule for the UHS plant

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A Appendix A

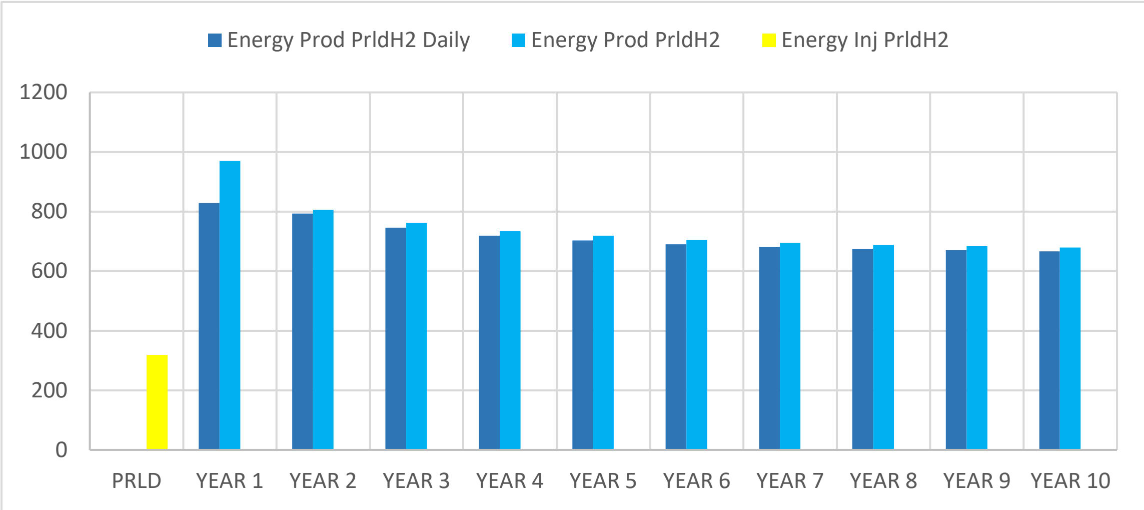


Figure A- 1: Energy Production Daily base schedule vs Base Case

Here an energy description of the Daily flexible case is given with respect to the base case, as already said in Section 5.6.2 less CO_2 comes out in the Daily case, hence less methane and less total Energy Production as showed in this Figure A-1

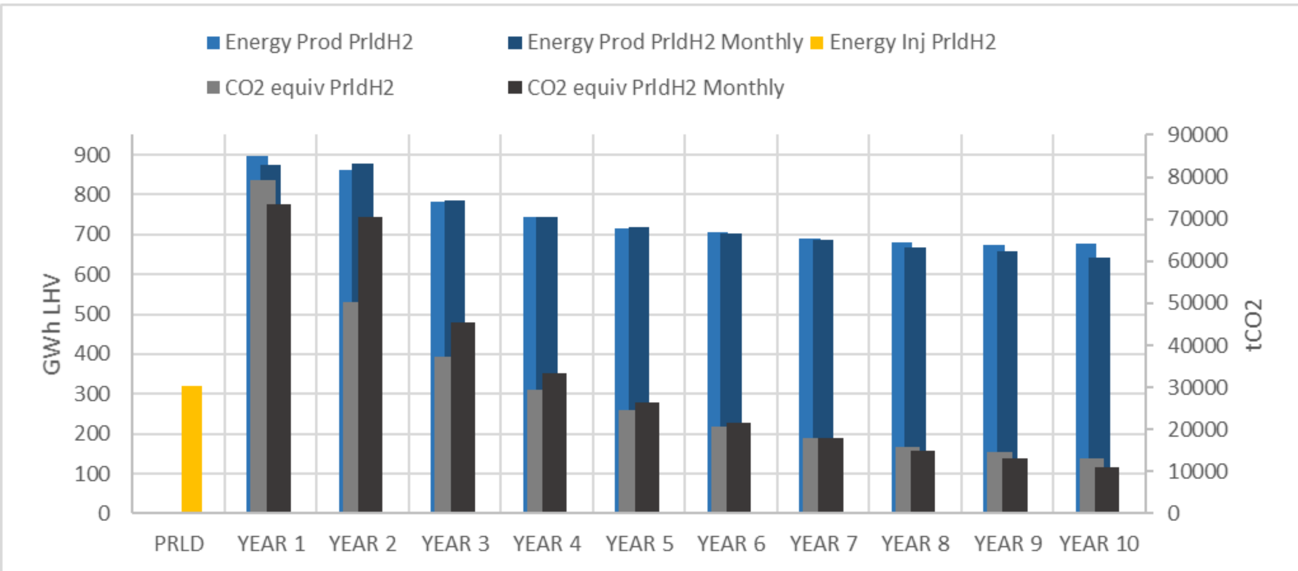
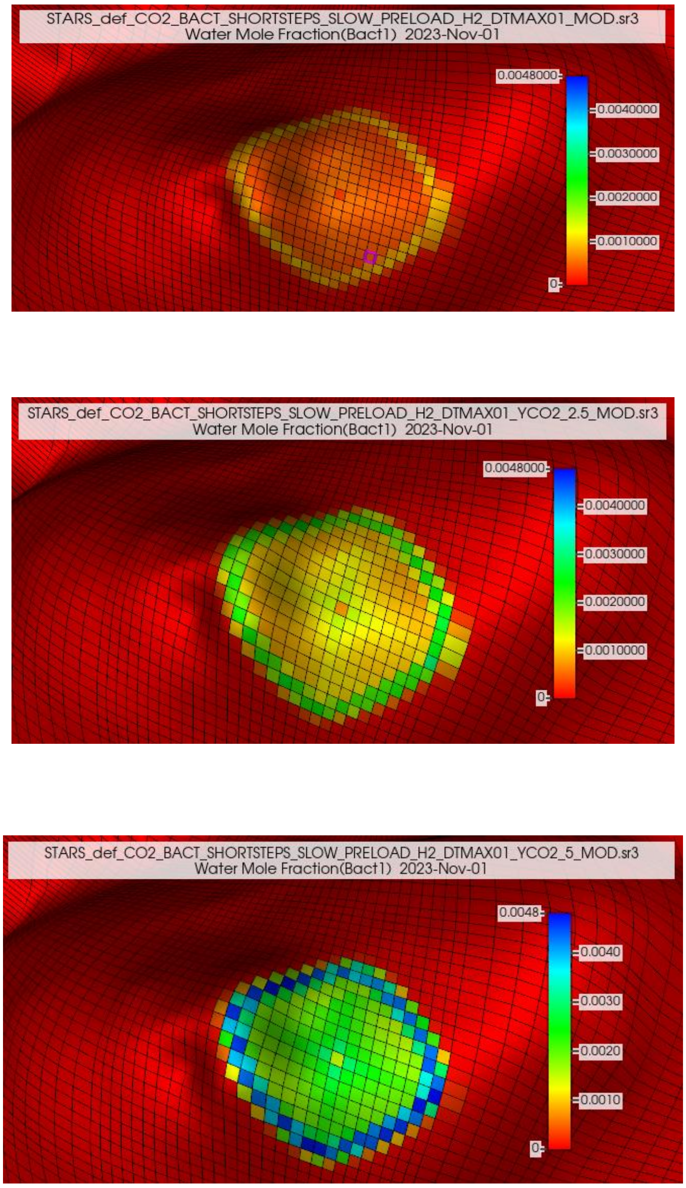


Figure A- 2: Energy Prod and tCO_2 equiv emissions Monthly based vs Base Case

Here Energy data together with tCO2 equiv emitted data are given. As stated in Section 5.6.1 limitations on BHP_min decrease the total Gas Production rate slightly bringing down the total amount of energy produced in the last years of operation with respect to the Base Case.



1%CO2

2.5%CO2

5%CO2

Figure A- 3: Different Methanogens Proliferation based on Initial amount of CO_2

This Figure shows how differently the methanogens proliferation occurs with respect to the initial amount of CO_2 present in the reservoir. The molar fraction scale used in the three different pictures is kept constant to highlight the phenomenon.

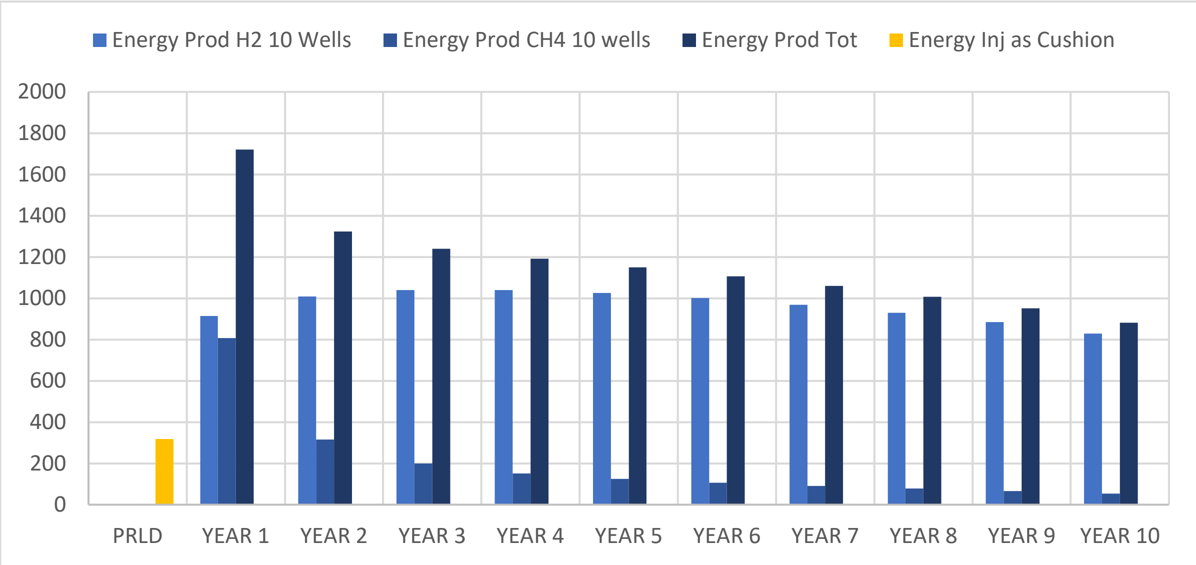


Figure A- 4: Energy Production for 10 wells in place: 1267.4 GWh_{LHVH2} injected

Here Energy data on the 10 wells case are given to further assess how the total capacity of the reservoir was estimated. As reported in the description the total energy injected per year was 1267.4 GWh_{LHVH2} and for the first time the energy produced by the facility became lower than the injected one. As reported in Section 5.5.2 this happens because wells reach the maximum water-gas ratio and are stopped for some periods of the year. This picture shows more details about the molecules coming out in the production stream: as expected methane is strongly present in the first years of operation and then its amount strongly decreases; the peculiarity of this figure is the energy production for hydrogen. For the first time this value has a decrease after few years of operation, once again this is due to the stoppage of the production wells due to techno-economic limits that finally suggested that this amount of gas injected was too much to handle for the reservoir level.

List of Figure

Figure 0-1: Thermodynamic vs Electrochemical Conversion to final Electric Energy .. 1
Figure 0-2: Photovoltaic and Total Load Curve in 2022 (GWh) 3
Figure 1-1: Hydrogen projected development in different industrial sector 8
Figure 1-2: Different Underground Hydrogen Storage (UHS) options.......................... 9
Figure 1-3: Carbon cycle and CO_2 management in a hydrogen-based economy 13
Figure 3-1: Gas Saturation for level L3 20
Figure 3-2: Historical Pressure and Gas Production Rate Data 20
Figure 3-3: Microorganism Proliferation in a Batch culture laboratory experiment ... 22
Figure 3-4: Result of Power-law tuning over the Monod model.................................. 26
Figure 4-1: Variable Parameters scheme for sensitivity analysis 30
Figure 4-2: Gas Production Rate Composition.. 30
Figure 4-3: Methanogenic Archaea final aqueous concentration distribution 32
Figure 4-4: Components aqueous concentration evolution 32
Figure 4-5: Gas Production Rate Composition – Methane as cushion gas.................... 33
Figure 4-6: Methanogenic Archaea final aqueous concentration distribution 34
Figure 4-7: Components aqueous concentration evolution 34
Figure 4-8: Gas Production Rate Composition – Carbon Dioxide as cushion gas 36
Figure 4-9: Gas Production Rate Composition – Different initial amount of Carbon Dioxide 37
Figure 4-10: Losses due to Methanogens Proliferation 38
Figure 5-1: Energy Production and CO_2 equivalent emissions 41
Figure 5-2: Molar Fraction trend 42
Figure 5-3: Injection schedule for Base Case 43
Figure 5-4: Production schedule for Base Case 43
Figure 5-5: Molar Fraction trend 44
Figure 5-6: Energy Production and CO_2 equivalent emissions 45

Figure 5-7: Pressure evolution during H_2 storage operations 45
Figure 5-8: Pressure evolution during H_2 storage operations 46
Figure 5-9: Injection schedule for Halved cushion gas amount 47
Figure 5-10: Production schedule for Halved cushion gas amount 47
Figure 5-11: Pressure evolution during H_2 storage operations 48
Figure 5-12: Injection schedule for Doubled cushion gas amount 48
Figure 5-13: Production schedule for Halved cushion gas amount 49
Figure 5-14: Molar Fraction trend 50
Figure 5-15: Pressure evolution during H_2 storage operations 51
Figure 5-16: Injection schedule for 7 Wells in operation 51
Figure 5-17: Production schedule for 7 Wells in operation 52
Figure 5-18: Production schedule for 10 Wells in operation 53
Figure 5-19: Schematic representation of the energy vector and CO_2 flows within one node 54
Figure 5-20: State of Charge projection for a UHS facility 55
Figure 5-21: State of Charge and Scheduled flowrate projections for Monthly based case 56
Figure 5-22 Production schedule for Monthly based Schedule 57
Figure 5-23: State of Charge and Scheduled flowrate projections for Daily based case 58
Figure 5-24: Gas Production rate evolution during a decade of operation 59
Figure 5-25: Bottom Hole pressure evolution of the 9th year of operation 59
Figure 5-26: Water Gas ratio evolution over a decade of operation 60
Figure 5-27: Pressure evolution during H_2 storage operations 60
Figure 5-28: CO_2 equivalent tons emitted: Daily vs Base case 61
Figure A- 1: Energy Production Daily base schedule vs Base Case 67
Figure A- 2: Energy Prod and tCO_2 equiv emissions Monthly based vs Base Case 67
Figure A- 3: Different Methanogens Proliferation based on Initial amount of CO_2 68
Figure A- 4: Energy Production for 10 wells in place: 1267.4 GWh_{LHVH2} injected 69

List of Tables

Table 1-1: Underground Hydrogen Storage Options Relevant Values [1] 9
Table 1-2: Existing and planned Hydrogen storage facilities for salt caverns 11
Table 3-1: Petrophysical properties of Nissa field 18
Table 4-1: k-value coefficients to be inserted in experimental correlation (4.1) 28
Table 4-2: Molecular Weight, Critical p and T, Viscosity Coeff. for eq. (4.2)................ 28
Table 4-3: Stoichiometric Coeff, Reaction Orders, Aqueous critical concentrations ... 29
Table 4-4: Well Dimensions and characteristics and Target Surface Flowrate............. 29
Table 4-5: Methanogens losses and Total losses for each cycle and for the 2 years 31
Table 4-6: Methanogens losses and Total losses for each cycle and for the 2 years 33
Table 5-1: External Constrains 40

List of symbols

Variable	Description	SI unit
ψ^{growth}	Microbial Growth Function	1/s
ψ_{max}^{growth}	Maximum Growth Rate	1/s
x	Molar fraction in water	-
α	Half velocity constant	mol/mol
ρ	Phase density	kg/m^3
v	Advective velocity	m/s
q	Instantaneous flux	m/s
K	Permeability of the medium	m^2
μ	Dynamic Viscosity	Pa*s
L	Specific length	m
p	Pressure	Pa
j	Dispersive/diffusive flux	$mol/m^2/s$
D	Diffusivity	m^2/s
y	Vapour molar fraction	-
x	Water molar fraction	-
k	Vapour-Liquid equilibrium constant	-
R	Reaction rate	-
F	Frequency factor	1/s
β	Component Reaction order	-
$\hat{c}$	Aqueous concentration	mol/l
Γ	Stoichiometric coefficient	-
Y	Yield coefficient	$cells/molH_2$

k_n	Number of bacteria per mole	cells/mol
n_b	Moles of bacteria	moles/m^3_{water}
T	Temperature	K
Q	Flowrate	Sm^3/d

List of Acronyms

Acronym	Description
NG	Natural Gas
RedOx	Reduction-Oxidation
GHG	Greenhouse Gas
PHS	Pumped-Hydro Storage
CAES	Compressed Air Energy Storage
PV	Photovoltaic
UHS	Underground Hydrogen Storages
COP	Conference of the Parties
CCUS	Carbon Capture Utilization and Storage
SR	Steam Reforming
WGS	Water Gas Shift
IEA	International Energy Agency
LHV	Lower Heating Value
UMR	Underground (bio)-Methanation Reactor
WP	Work Package
LCA	Life Cycle Assessment
M	Methanogenic Archaea
A	Homo-acetogenic Archaea
SRB	Sulphate-reducing Bacteria
IRB	Iron(III)-reducing Bacteria
SoC	State of Charge
OMNI-ES	Optimisation Model for Network-Integrated Energy Systems

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Fosso Drittolo Crew

FANTA-CARLETTO

LA SQUADRA

I DISGRAZIETI

(Be careful)^n

Three Italians and Three Germans in Norway

Viscontini Elite mista

Credo che ognuno di loro possa riconoscersi in almeno uno di questi gruppi, grazie.