Chapter 1

Introduction

Within the last decade, an increasing shift from fossil fuels to renewable energy sources is evident with respect to the global climate movement. In Germany, the share of renewable energy sources of the electrical energy supply in 2021 was 43.9 %, where wind power delivered the main contribution of renewable (∼50 %), followed by photovoltaic (∼24 %), and biomass (∼17 %) [4]. Typically, the supply from renewable energy sources such as wind and solar is subject to fluctuations seasonally but also daily. A similar behavior is also observable for the energy demand, although the oscillation often differs significantly, leading to an increasing importance of energy buffers in a sustainable energy system for the future. Here, converting excess electrical energy into other energy carriers such as hydrogen, methane, and ammonia, which can be subsequently consumed when demanded, is regarded as a suitable solution (cf. Figure 1.1). This concept is called Power-to-X, whereby the X relates to the form of energy or usage (e.g. power-to-heat, power-to-gas, and power-to-liquid). Recently, hydrogen has been a promising candidate within the field of power-to-gas due to its versatile usage as an energy carrier and resource for various industries.

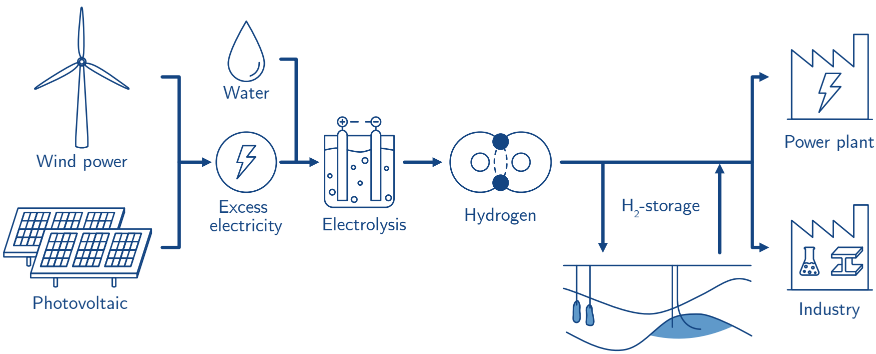

Figure 1.1: Workflow of the power-to-gas concept with hydrogen as energy carrier

Using hydrogen as a renewable energy carrier and simultaneously as a valuable resource for industries such as steel and chemicals will increase the overall demand in the following centuries. In 2019, Hebling et al. [59] prognosticated a hydrogen demand within a range of 250 TWh to 800 TWh for Germany by 2050 (800 TWh to 2250 TWh for Europe). Recent predictions are higher with an overall hydrogen demand of up to 1000 TWh for Germany and more than 4000 TWh for the entire EU by 2050 [51] (cf. Figure 1.2).

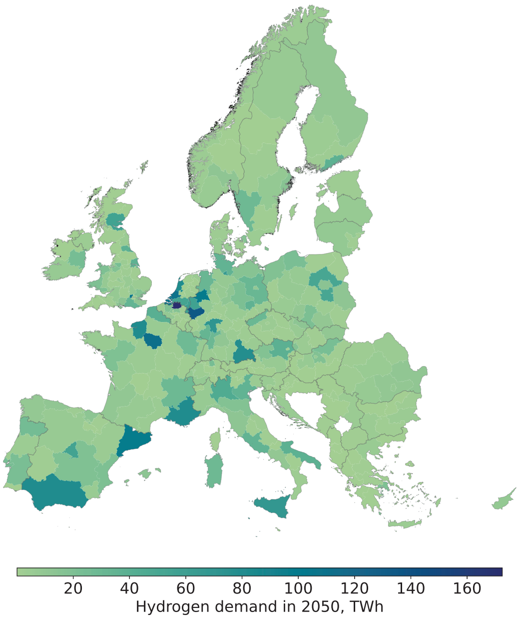

Figure 1.2: Overview of hydrogen demand by year 2050 [51]

Contemporary studies expect a storage capacity of 20 % to 30 % of the annual hydrogen demand [52]. The highest potential for renewable energy production and the use for hydrogen generation is located offshore (wind power) and in the southern part of Europe to the African region, which leads to large transport distances between producer and consumer [51]. Projects such as the European Hydrogen Backbone [154] are investigating the establishment of a European-wide reliable hydrogen pipeline grid and transportation system.

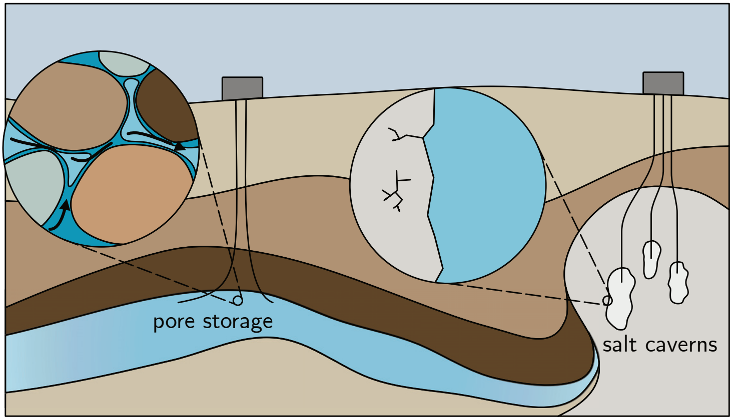

Figure 1.3: Overview of storage types - Stored fluid indicated with ■

Nevertheless, the fluctuations in demand and supply of energy and the geopolitical dependency lead to a more dominant role of energy storage in the future. Nowadays, energy storage in larger quantities is mainly performed by injecting natural gas and other hydrocarbon fuels into the subsurface, from which they can be withdrawn later. Generally, two types of underground gas storages (UGS) (cf. Figure 1.3) are used:

- Storage of gases and liquids in caverns, typically leached in salt formations such as salt diapers: Salt formations are crystalline rock entities usually with ideal sealing capacities. Typically, this type of storage allows high deliverability and hence is suitable for the short-term balance, allowing several storage cycles per year [85]. Due to their comparatively low capacities (geometrical size: 30 000 Sm^3 to 500 000 Sm^3) [144], caverns are often arranged in clusters. However, this type of storage is only feasible in regions with salt formations (e.g. Northern Germany), and therefore, their potential is limited.

- The cyclic injection and withdrawal of gases in porous and permeable rock formations, mainly depleted gas/oil fields: The storage formation composes a structural trap, where the cap rock prevents the migration of fluids to higher formations due to its extremely low permeability in combination with the capillary threshold pressure [78]. Typically, larger capacities can be observed, allowing seasonal storage, and due to the higher availability of suitable porous formations [85], the importance of this type of storage is significant with an increasing demand for storage capacities globally. However, the porous medium only allows lower injection and withdrawal rates per well than caverns and hence has only a limited contribution to short-term storage [144].

Overall, the coexistence of both storage types is favorable and behaves symbiotically to store energy and balance the changes in demand and production on a daily but also seasonal basis. In this study, the storage of fluids in porous rock formations is in focus due to its increasing importance regarding the growing hydrogen infrastructure. An overview of the history and current research on the storage of gases containing hydrogen in the subsurface is presented in the following. The concept of Underground Bio Methanation, derived from UHS, is also introduced.

1.1. Underground Hydrogen Storage

The storage of energy in the subsurface has more than 100 years of history. A first attempt to store natural gas in a depleted gas field was successfully carried out in Ontario, Canada, in 1915 [39]. The significance of subsurface energy storage increased over time, ensuring a consistent energy supply during low-production and high-demand periods. First storages for pure hydrogen were established in caverns to store hydrogen for petrochemical industry applications [87]. Initial experiences with storing hydrogen in porous formations were gained during the storage of hydrogen-rich town gas in Ketzin (Germany), Beynes (France), and Lobodice (Czech Republic) in the period between the 1950s and 1980s [100, 133]. With the growing interest in a carbon-free energy economy over the last century, the idea of storing green hydrogen in the subsurface gained traction, leading to research projects in both fundamental research and pilot phases.

In the 2010s, national research projects were initiated to improve the fundamental knowledge of UHS. Addressing the efficiency of the storage process, the research project *H2STORE* (2012 to 2015) [43] investigated the transport process in porous media and potential contamination due to microbial activity in numerical simulations. In the follow-up project *HyInteger* (2016 to 2019) [44], the attention was mainly placed on barrier elements, such as weakening wellbore components like cement and steel, and potential impacts on the formation by geochemical reactions. After performing laboratory experiments with wellbore materials at reservoir conditions, the risk of the hydrogen-induced integrity issues was concluded to be insignificant.

Aside from nationally funded research projects, also international projects were initiated to assess the technical feasibility of a large scale UHS strategy. Two relevant activities are the EU projects *HyStorIES* (2021 to 2023) [48] and *HyUSPRe* (2021 to 2024) [104]. Within these projects, various laboratory experiments (microbiology, geochemistry, geomechanics, and gas-gas mixing behavior) were conducted to tune field scale simulation models. Subsequently, these simulation models were used to identify potential risks and define guidelines for the operation. In addition to the technical assessments, economic studies and challenges regarding the general public acceptance were conducted.

Besides theoretical and laboratory investigations, first field tests were conducted to assess the feasibility of UHS. In 2013, RAG Austria AG initiated the research project *Underground Sun Storage* [126] addressing the storage of a hydrogen blend (up to 10 % of hydrogen) in a depleted gas field in Austria. The project began with fundamental investigations to assess potential impacts on storage integrity, with no direct issues observed. Subsequently, the planning, permission, installation, and operation of the UHS test followed. By the end of the pilot phase in 2017, a total amount of $1.22 \cdot 10^6\,\mathrm{Sm}^3$ of the hydrogen-natural gas blend was injected into the formation, with 18 % remaining stored after withdrawal. Notably, there were no hydrogen-related abnormalities during the operation [126]. The activity was continued within the project of *Underground Sun Conversion* (2017 to 2021) [124], and since 2023, the operation of UHS with pure hydrogen in a separate location is investigated within the follow-up project *Underground Sun Storage 2030* [125].

Almost parallel to the activities in Austria, the Argentinian company *Hychico* S.A. initiated a project focusing on the generation of renewable hydrogen followed by the injection into a depleted gas field in 2013 in cooperation with the French research organization BRGM [117]. However, the final outcomes of the project are still unpublished.

In the middle of 2023, the German company Uniper SE started the injection of a natural gas blend with hydrogen concentrations between 5 % to 25 % into a sandstone formation in Bavaria, Germany, within the project of *HySTORAGE* [141]. In three phases, the impact of gas-gas mixing with the initial gas and potential losses due to microbial activity will be assessed. The project is planned to be finished by 2025.

1.2. Underground Bio Methanation

During the storage of hydrogen-containing town gas, changes in fluid composition were observed. The observations were a decreasing hydrogen and carbon dioxide content with a simultaneous increase in the methane content. Later on, this shift was accounted to methanogenic microorganisms. This effect is unfavorable during UHS as a high purity of stored hydrogen is aimed. However, in the concept of Underground Bio Methanation/Underground Methanation Reactor (UMR), these methanogenic microorganisms are used to metabolize hydrogen and carbon dioxide in a 4:1 ratio to produce methane and water, which can remain in the storage and be withdrawn on demand [110]. Figure 1.4 shows a schematic overview of the concept with a doublet well setup where the conversion occurs during the flow from the injector to the producer well. The benefits of this idea are that the existing infrastructure

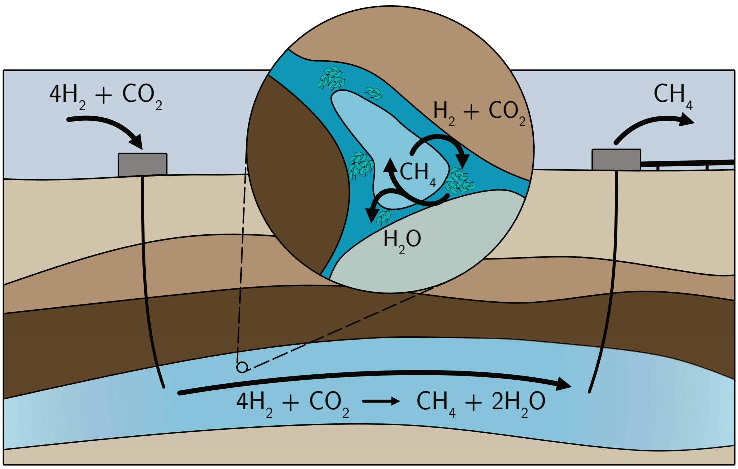

Figure 1.4: Schematic overview of the concept of an Underground Bio Methanation Reactor (UMR)

for natural gas can be utilized and that methane has a higher energy density than hydrogen, making this concept capable of higher energy storage capacity than a pure UHS.

Technology concepts are often classified by their technology readiness level (TRL) [35], categorizing the maturity of their progress. The TRL of UMR can be classified as TRL3, where the general concept is formulated and experimental proof has been provided. The experimental proof was achieved through a combination of laboratory experiments and conclusions from field tests. Research projects such as *BioUGS* [77] mainly focused on the growth kinetics of the microbial species in batch reactors (bulk) to estimate the resulting efficiency. The research activity *CliMb* (2019 to 2022) focused not only on the pure growth kinetics but also on the impact of the porous media and influences on the transport process. Overall, it proved the significance of the species present in the formation and the required environmental conditions to enable the potential of UMR on larger scales. With the initial intention of preceding investigations for a pilot phase, the project *UMAS* (2020 to 2022) [101] investigated the techno-economic assessment of a UMR in a former UGS in Germany. However, growth experiments indicated a complete inhibition of microbial growth due to the high salinity of the brine, which prevented the field case study [101]. In direct comparison, the previously mentioned UHS projects *Hychico* and *Underground Sun Conversion* were used to investigate the potential application as UMR where in both cases microbial activity led to the striven for conversion to methane [117, 124]. Within the activities of *Underground Sun Conversion*, a natural gas-hydrogen-carbon dioxide blend was injected (up to 20 % H_2) in the stoichiometric ratio (H_2:CO_2 4:1) to promote the microbial activity. Although a conversion could be observed, it fell short of expectations [124].

1.3. Motivation and objectives

The need for large-scale energy storage systems with an increasing share of renewable sources is evident. Storing hydrogen in the porous subsurface could contribute to this energy system significantly. However, the introduction of hydrogen can cause various phenomena. Numerical reservoir simulation is a powerful tool to model and predict the transport processes in porous rocks. In recent years, various simulations for UHS have been conducted. Regarding the field scale, most simulations focused on pure transport affected by different thermodynamic properties and hysteresis of relative permeability curves [15, 92], which have been observed in the laboratory. Additionally, simulation studies have been applied to evaluate operational designs, such as different types of cushion gas and well configurations [25, 33, 57]. However, these studies have often neglected hydrogen reactions, which are significant for particular storages. In 2018, Hagemann [54] developed a mathematical model with subsequent numerical implementation in the open-source simulator DuMu^x to predict the reactive transport process during hydrogen storage in the porous subsurface. This study's focus was modeling potential biochemical reactions caused by microorganisms being present in the pores of the rock. Regarding implementations in commercial simulators, simplified growth models were incorporated in some simulators [79, 157]. Focusing on the implementation of Hagemann [54], the work was primarily based on literature observations and lacked calibration with actual laboratory investigations. Other reactions, such as geochemical reactions, which could impact UHS efficiency, were not considered, and the analysis of gas-gas mixing between injected and initial gases was performed, but it relied on simplified thermodynamic properties (e.g. ideal gas law).

To address these limitations and enhance the existing implementation in DuMu^x, the following objectives were defined:

- Extending the existing simulation model by geochemical reactions (pyrite-to-pyrrhotite reduction) to predict the impact on UHS and introduce more applicable correlations regarding thermodynamic properties for the expected high pressure and temperature conditions.

- Calibrating the developed bio- and geochemical simulation model by matching laboratory observations regarding microbial growth parameters, geochemical reaction kinetics, and the gas-gas mixing by molecular diffusion to the model for subsequent field scale application.

- Extending the modeling approach of mechanical dispersion to predict the gas-gas mixing more reliably in DuMu^x with subsequent prediction for a pilot UHS project.

- Testing the applicability of the developed implementation in DuMu^x to model freshwater injection to enable UMR in high-saline aquifers.

Achieving these objectives culminates in an improved numerical implementation, which allows for better certainty in predicting the processes during UHS. The model is accessible for public use on an open-source basis and is available to increase the efficiency of UHS through optimized operation.

1.4. Outline of the thesis

This thesis comprises six chapters and is structured as follows:

Chapter 2 depicts the fundamentals of relevant physicochemical processes related to the storage of hydrogen-containing gases within the subsurface based on a literature review. Particular focus is placed on hydrodynamics, biochemical, and geochemical reactions potentially influencing the efficiency of the storage process. Furthermore, this chapter provides the fundamentals of modeling two-phase multi-component transport in porous media, including the generalized mathematical model and its realization numerically.

In Chapter 3 an existing mathematical model for bio-reactive transport during UHS is extended by geochemical reactions (pyrite-to-pyrrhotite reduction) and consecutively implemented in the open-source simulator DuMu^{x}. Significant attention is placed on the calibration of the gas-gas mixing caused by molecular diffusion bio- and chemical reactions by recent laboratory experiments. The experiments are reproduced on a laboratory scale within simulations to achieve this calibration. In the final step, the developed and calibrated model is applied to a previously developed benchmark scenario for UHS to assess the risk on a larger scale.

Chapter 4 comprises the extension of the bio-reactive transport model concerning the gas-gas mixing caused by mechanical dispersion. Focusing on field scale simulations with conventional reservoir simulation grids, among other things, modifications in spatial discretizations and well modeling are required. The developed model is subsequently used to predict an ongoing pilot operation of UHS in Germany.

Within Chapter 5, the bio-reactive transport model is applied to predict the stimulation of microbial growth aiming for UMR. To counteract the inhibiting impact of high salinity brine on microbial growth, freshwater is injected, enabling the targeted growth of methanogenic archaea. To simulate this study, the microbial growth kinetics are extended by the influencing parameter of salt. Afterwards, a sensitivity study of microbial growth parameters and freshwater volume is performed.

Chapter 6 contains an overview of relevant conclusions from the results obtained in the previous chapters.