Chapter 1

Introduction

The idea of taking hydrogen as the energy carrier for a renewable energy supply system can be traced back to the early 20th century. In February 1923 the Briton J.B.S. Haldone hold a speech at the Cambridge University where he suggested a power supply system based on hydrogen producing windmills [61]. This idea was continued by J.O. Bockris who published the first article about a so-called “hydrogen economy”, where energy is stored and distributed in the form of hydrogen gas, in 1972 [17]. A new impulse is given by the change from nuclear to renewable energy in many European countries which demands an increasing amount of storage capacities for electrical energy [44]. The renewable energy supply which is generated primary by wind and solar power plants is strongly fluctuating. The reasons are changing weather conditions which take place in different time scales [29]. It is possible that long times of recession in the energy production have to be bridged. Additionally, the demand of electricity also varies on a daily and seasonal time scale [70]. The balance implies the temporal storage of electricity wherefore several storage options are currently under discussion. Battery storages have a high energy density but they are cost-intensive [83]. Compressed air energy storages and pumped hydro storages, where the energy is stored as potential or compression energy, have a relatively low energy density of 0.7 to 3 kWh/m^3 [70]. These options are preferred for the short term storage, the so-called minute and hour reserve [70]. Underground hydrogen storages (UHS), where the energy is stored as chemical energy, have an energy density which is higher by two orders of magnitude [70]. Consequently, they provide the possibility to store electrical energy in the long term or even seasonal period [29]. The technology comprises an electrolyzer which uses excessive electrical energy to split water into oxygen and hydrogen [70]. Different concepts for the subsequent storage and usage of hydrogen are available [91, 45, 29]:

- ”POWER-to-GAS”: The produced hydrogen will be fed into the existing natural gas grid. Investigations have shown that concentrations in the single-digit percentage area are supposable [36]. This means that also the existing underground gas storages will be charged with natural gas containing low percentages of hydrogen.
- ”POWER-to-GAS-to-POWER”: The hydrogen is stored purely in subsurface formations such as depleted gas or oil reservoirs, aquifers and solution mined caverns [111]. At times of energy demand the hydrogen is withdrawn and can be used as energy fuel for stationary fuel cells or engine-generators connected to the electrical grid or for fuel cell vehicles.

1.1 Motivation

In September 2010 the German Federal Government announced a new energy concept [44]. The objectives are essential changes in the energy supply until the year 2050 [44]:

- A reduction of greenhouse gas emission by 80-95%
- An expansion of renewable energy supply by 60%
- A reduction of the primary energy consumption by 50%

A critical interface for these targets is the storage of electrical energy [44]. The increasing share of renewable energy results in strong fluctuations in the electricity generation [44]. Consequently, large buffers are required to balance the base load and additional reserves need to be provided for peak shaving. However, the realization is detained by technical aspects [44]. For the promotion of applicable technologies the ”funding initiative energy storages” was started in 2011 by the Federal Ministry for Economy and Technology, the Federal Ministry for Environment, Nature Conservation and Nuclear Safety and the Federal Ministry for Education and Research. The initiative has a budget of €200 Mio. and supports research and development projects in the area of electrical, substance-based and thermal storages [44]. The projects span from fundamental research to economic efficiency improvements [44]. A substantial part of this intention is on UHS which is currently regarded as a promising solution for the large scale storage of electrical energy. However, UHS is an unexperienced new technology and the suitable technical and geological conditions need to be determined before an UHS can be placed into operation. The supported research projects should make progress in this area which brings the implementation one step closer. This includes the project H2STORE which was carried out from 2011 to 2015 and HyINTERGER which is subsequently carried out until 2018, both partly at the Institute of Petroleum Engineering (Clausthal University of Technology) and the University of Lorraine, France. Also involved in these projects are the University of Jena and the GFZ Potsdam, both in Germany.

1.2 Underground hydrogen storage

The term ”underground hydrogen storage” refers to the cyclic storage of hydrogen gas in subsurface formations as similarly done with natural gas. The cycle starts with the production of hydrogen from excessive electrical energy. Pressure electrolyzers are used which split water into hydrogen and oxygen [70]. Subsequently, gas installations with compressors are required to further compress and transport the hydrogen to the wells. The hydrogen continues to flow from surface into a geological formation through these wells. Within the storage formation, it remains until it is withdrawn during times of energy demand. At surface the pressure is released and in some cases a gas processing is required before the hydrogen is again available as energy fuel [70].

In this process the geological formation has to meet some basic requirements:

- An adequate volume need to be provided to store large amounts of hydrogen
- The structure need to be enclosed to prevent losses in the adjacent rocks
- Its properties have to allow the injection and withdrawal at efficient rates

Two different options come into consideration: solution-mined salt caverns or porous rock formations such as aquifers and depleted gas/oil reservoirs.

Salt caverns are large void spaces which can be created in bedded or domed salt formations by a solution mining process [121]. The advantage is that salt rock features a very high gas tightness and therefore losses can be practically neglected [29]. Additionally, the injection and withdrawal rates are only limited by the wells and legal regulations [29]. Consequently, they are well suited for several storage cycles per year. The operation is typically done by compressing and decompressing the gas within a defined pressure range [29]. Thereby a portion of the gas remains in the cavern, the so-called cushion gas. The usable amount of gas volume is defined as working gas. For an ordinary salt cavern with a geometrical volume of $500,000\ m^3$ and a maximum pressure of $200\ bar$ the working gas volume is around $6 \cdot 10^7\ Sm^3$. The large hydrogen volume, which is required as cushion gas, represents a significant upfront investment.

Capable porous rock formations consist of a high porous and high permeable geological structure which is covered by an almost impermeable cap rock [111]. Additionally, a trap structure is required which prevents the migration of gas. The difference between aquifers and depleted reservoirs is mainly given by the initial pore filling. Aquifers are saturated only by water whereas depleted reservoirs can be saturated by up to three phases including gas and oil. However, an imperfect structure or possible reactions of hydrogen with minerals and microorganisms can result in some gas losses [70]. The injection and withdrawal rates are limited by the permeability and therefore the number of storage cycle per year is restricted [111]. In this case again, a certain amount of gas always remains in the storage as cushion gas. The advantage is the high volume of these structures which allows a storage of more than $10^9\ Sm^3$ [111]. Additionally, the availability of these structures is not limited to minor regions in Germany. The storage in depleted gas reservoirs will not require large hydrogen volumes as cushion gas, but the produced gas will not contain pure hydrogen.

1.3 State of the art (applications)

The concept of storing gases in the underground is established since almost 100 years [111]. Although the experience is limited to natural gas and gas mixtures, the storage of hydrogen can be treated similarly in many issues [111].

The VDE association [80] reports an unproblematic storage of pure hydrogen in salt caverns. Such facilities are under operation since decades in Teesside, United Kingdom and Texas, USA to store hydrogen for the chemical and petrochemical industry [80]. The gas leakage is below 0.02% per cycle [80].

Operational experiences for porous media storages are only gained for hydrogen mixed gases such as town gas. The DVGW [90] reported some problems during the storage of town gas in depleted reservoirs and aquifers. An enormous reduction in the gas volume was observed whereby leakages through the cap rock and wells could be excluded [90]. The cause has not been clarified definitively. The detection of sulfate-reducing bacteria allows the assumption that microbiological induced reactions are accountable for the gas reduction [90]. However, not all town gas storages were affected and the experiences can not be transferred directly to UHS [90].

An unexpected behavior was also reported for the town gas storage in an anticline aquifer structure near Lobodice, Czech Republic. During a storage cycle of seven months a drastic increase in the CH_4 concentration and a decrease in the CO, CO_2 and H_2 concentrations as well as changes in the gas volume were reported [118, 21]. Smigan et al. [118] analyzed the existence of methanogenic microorganisms in the stratal water and concluded that microbiological induced reactions could be responsible for the methane enrichment.

The Argentinian company Hychico S.A. started a pilot test in 2013 [114]. They added hydrogen as tracer to the natural gas stream and stored the gas mixture in a depleted gas and oil field. Results of this test are unpublished so far.

RAG Austria (Rohöl-Aufsuchungs Aktiengesellschaft) started a pilot test in 2015 [12]. They were injecting a gas mixture of natural gas with 10% hydrogen into a small depleted gas reservoir in Austria. The back production will started in summer of 2016. Results of the field test will be available in spring 2017.

1.4 Recent related research projects

The topic of hydrogen as energy storage or transfer medium increasingly attracts the worldwide interest. Many research projects were launched during the last 5 years to investigate and advance the different sections in the chain of hydrogen production, storage, transport and usage. Thereby the large scale storage of hydrogen is an important connection which is currently focused by several research projects.

1.4.1 H2STORE

The H2STORE project started in the mid of 2012 and ran until the end of 2015. It was a joint research project with project members from University of Jena, Clausthal University of Technology, GFZ Potsdam and University of Lorraine. The initiator was the Federal Ministry for Education and Research in the context of the funding initiative for energy storages. H2STORE aimed to investigate the feasibility of large scale hydrogen storage in porous geological formations [46]. Thereby the focus was on depleted gas reservoirs in Germany [46]. The project was divided into six sub projects which are based on laboratory experiments, numerical simulations and analytical work [46]. The field of activity covered the investigation of mineralogical, geochemical, physio-chemical, sedimentological, microbiological and gas mixing processes in reservoir and cap rocks [46].

1.4.2 HyUnder

The HyUnder project also started in the mid of 2012 and ran for a total time of two years. The list of project partners comprises 12 organizations from 7 countries: Germany, France, United Kingdom, Spain, Netherlands, Romania and Belgium [20]. The participators are small to large industrial companies and research institutes [20]. HyUnder purposed to assess an implementation plan for UHS in the European Union [20]. The different working packages include a benchmarking against other large scale storage options, investigating the different geological formation options, mapping potential storage sites in Europe, simulating and comparing different case studies [20]. The results show the technical, economic and prospects of UHS [64].

1.4.3 Hychico

Hychico S.A. started one of the first field trials on the way to an UHS deployment. The Argentinian company was founded in 2006 by partners from the field of energy resources. Since 2009 they are running a hydrogen pilot plant in Diadema, Argentina [114]. The plant consists of two electrolyzers which are using the power from an attached wind park to split water into hydrogen and oxygen [114]. Subsequently, the high purity hydrogen is mixed with natural gas and combusted in an engine-generator whereby electrical power is regained [114]. The oxygen is stored at surface and sold to the industrial gas market [114]. Until now, Hychico was able to successfully test their energy conversion cycle [114]. Starting in 2013, the feasibility of storing hydrogen in a nearby depleted oil and gas reservoir was tested [114]. Thereby, hydrogen was injected as a tracer admixed to natural gas [114]. The storage of pure hydrogen is also planned [114].

1.4.4 ANGUS+

The ANGUS+ project started in the mid of 2013 and was completed in 2015. It was conducted by the University of Kiel and partners were UFZ Leipzig, GFZ Potsdam and Ruhr University Bochum [11]. Like the H2STORE project it was financed by the German Ministry of Education and Research in the context of the initiative for energy storages [11]. The project focused on the spatial interferences between different subsurface usages [11]. Thereby, the concentration was set on the storage of natural gas, synthetic methane, hydrogen and compressed air in caverns and porous media as well as the storage of heat [11]. The objective was the development of geological fundamentals for these storage types and also economical, political and legal conditions were considered [11].

1.4.5 Underground Sun Storage

The research project ”Underground Sun Storage”, which was initiated by the Austrian company RAG, started in 2012 [12]. Project partners are the Montan University Leoben, University of Natural Resources and Life Sciences Vienna, Johannes Kepler University Linz, VERBUND AG and Axiom Angewandte Prozesstechnik GmbH [12]. The project aims to investigate the feasibility of storing natural gas or synthesized methane with added hydrogen in porous underground storages. Within the 10 working packages it is planned to analyze the reservoir engineering, economical, legal and material characteristic aspects of UHS. Particularly interesting is the in-situ field test which involves the operation of one storage cycle with added 10% hydrogen [12].

1.4.6 HyINTEGER

HyINTEGER is the follow-up project of H2STORE which started in January 2016 with a duration of 3 years. The project consortium is the same as in H2STORE, additionally the University of Mainz has joined. The five sub projects aim to further investigate the chemical-mineralogical, microbiological and petrophysical-geohydraulic-geomechnical processes in reservoir and cap rocks whereby especially the interactions between technical and natural components of an UHS are considered. An additional aspect is the material behavior under the strongly corrosive conditions. Again the work is based on laboratory experiments, numerical simulations and analytical methods. The modeling part concerns the near-wellbore region, however, also an upscaling to field scale is planned.

1.5 Outline of the thesis

The thesis is structured as followed:

Chapter 2 is a literature review about the hydrodynamic and microbiological effects which can appear in UHS. Additionally, it contains a review about mathematical models which were developed to describe these effects in UHS or similar applications. The chapter summarizes decisive physical, chemical and biological processes in UHS and provides the background for the development of the mathematical model.

In chapter 3 the gravity-driven displacement is modeled analytically when hydrogen is injected to the bottom of a water saturated reservoir. The analytical solution was obtained by combining the method of characteristics with a graphical construction. Comparisons are also shown to the numerical solution.

In chapter 4 the development of a mathematical model for the bio-reactive transport in UHS is described. The model is based on continuum scale and couples compositional two-phase flow with bio-chemical reactions and microbial growth and decay within the porous medium.

In chapter 5 the stability of the mathematical model is investigated. Therefore, the equation system is reduced to a set of ordinary differential equations or a set of reaction-diffusion equations by appropriate assumptions. Based on the results, numerical simulations were performed which show different oscillatory regimes.

Chapter 6 covers the numerical implementation of the mathematical model which was done on the basis of DuMu^X (an open-source C++ code for the simulation of multi-phase multi-component flow and transport in porous media). The chapter includes numerical studies in two-dimensional conceptional and three-dimensional realistic geological models. The simulated scenarios include the development of the storage and the subsequent cyclic injection and withdrawal over several years.

In chapter 7 the results from all chapters are concluded.