Reports WP 5
D8

WP 5 Large-Scale Storage of Gases in Geological Storage Facilities

D8 **Report on the metrological and thermodynamic issues in the large-scale storage of hydrogen in UGS and the conversion of existing UGS from natural gas to hydrogen including the simulation of the flow behaviour of hydrogen / natural gas mixtures.**

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1 Introduction

1.1 WP 5 in the MefHySto-Project - Large-Scale Storage of Gases in Geological Storage Facilities

Hydrogen is seen as an important energy source of the future in politics and business worldwide. In various countries beyond Europe clear targets have been defined for the energy transition towards Hydrogen. In order to secure supply underground storage of Hydrogen is increasingly becoming the focus of politics and business. There is nowadays a great deal of experience worldwide in the storage of natural gas to meet medium-term demand and it is expected that some of this experience can be transferred to the storage of Hydrogen.

There are basically two storage options for storing Hydrogen in the geological subsurface:

- Pore storage (aquifers or depleted natural gas reservoirs) and
- Underground cavern storage (salt caverns or rock caverns).

Currently some 662 UGS facilities are in operation worldwide. Out of them 72 % are deployed in depleted hydrocarbon reservoirs, 15 % in salt caverns and 15 % in deep aquifers [16]. In Europe more than 100 underground gas storages (UGS) exist. For example, there are 49 ones operating currently in Germany, being porous structures used predominantly. However, so far no Hydrogen or Hydrogen mixtures are stored there. In contrast, storage in caverns is practiced only at a few selected locations (e.g., Teesside; 95 % H2 + 3–4 % CO_2) and mainly for use by the chemical industry.

There is already a long experience accumulated through many years in handling Hydrogen mixtures in underground storage facilities. This concerns mainly city gas (50 % H_2, 50 % CO), which has been stored underground in various types of storage facilities. This yields confidence on the feasibility of underground Hydrogen storage, at least, in principle.

Projections of UGS demands for Hydrogen are still uncertain. In general, the required total UGS-Hydrogen working volume would be in a range of 580 – 600 bcm and this is similar or slightly greater than the total working volume of UGS today.

When discussing about USG, a distinction must be made between storing pure Hydrogen in new caverns or Hydrogen-natural gas mixtures. Furthermore, because of the large investment necessary for new storages, the use of existing gas storage and thus the successive transition to Hydrogen is currently seen as the most realistic option.

The aim of this MefHySto work package, WP5, is to tackle metrological and thermodynamic issues in the large-scale storage of Hydrogen in underground gas storages and the conversion of existing UGS from natural gas to Hydrogen. WP5 will provide missing information on the thermodynamics in UGS studies. Additionally, it will develop and evaluate measurement methods for the conversion and subsequent use of the UGS for Hydrogen.

1.2 WP 5 tasks

The measurements on underground gas storage tanks are well established. There is extensive knowledge about their scope and measurement technology. Hydrogen changes things considerably regarding natural gas. Accordingly, tasks were defined in the project so that, on the one hand, served to describe the problem and, on the other hand, identified potential solutions. The specific aims of each Task are:

Task 5.1. To define the necessary metrological requirements for the introduction of Hydrogen in storage

Task 5.2. To measure storage-relevant impurities and traces of hydrocarbons in Hydrogen with existing and new GC methods

Task 5.3. To address current flow measurement issues for measuring Hydrogen and natural gas mixtures in existing gas grids based on the simulation of the behaviour of Hydrogen and Hydrogen mixtures (ratios 20/80; 50/50; 80/20) in existing measuring sections.

The work carried out is described in the following chapters.

2 Metrological and thermodynamic issues in the large-scale storage of hydrogen in UGS and the conversion of existing UGS from natural gas to hydrogen

2.1 Metrological and thermodynamic properties of UGS

The pure hydrogen is fed into the existing large-scale natural gas pipelines. Consequently, a mixture of both gases is then transported into the UGS [1], [2], [3].
The process of mixing as well as the dynamics of mixture along the pipeline and in the reservoir is under intensive research because of its influence on operational requirements, measurement of gas flow rate, changes in fluid transport processes, biogeochemical interactions and possible safety risks [2]. The basic requirements on UGS are:

- To accept gas from transport pipeline for injection into the reservoir
- To deliver high-quality gas to the distribution system
- Compliance with safety rules and prevention of gas leakage from the reservoir

Most common UGS failures are:

- Loss of reservoir integrity
- Loss of well integrity

Hydrogen properties in relation to UGS issues

Hydrogen occurs as a diatomic gas molecule (H_2) with a density of 0.089 kg/m^3 at standard temperature (25 °C) and pressure (1 bar). The small size of hydrogen molecules is the reason for high penetrability and a higher diffusivity in solids than other gases like methane display. The density of hydrogen is about 8 time less than the corresponding density of methane. Consequently, more space or pressure is required to store the same amount of gas. On the other hand, the lower hydrogen viscosity and molecular weight can contribute to leakage. From the aspect of operational safety, hydrogen is flammable and dangerous similar like natural gas. However, hydrogen has a lower flashpoint that indicates its wider range of flammability. More physicochemical properties of hydrogen can be found in [1].

Challenges of hydrogen storage in UGS

The main challenges directly result from the low volumetric energy density (resulting in requirement of considerably high pressure which in turn is supporting leakage), the low size of hydrogen molecules (resulting in diffusion loss, causing issues with UGS integrity) and finally from the chemical aspects of hydrogen interactions with other materials (possibly contributing to reservoir and pipelines degradation).

The hydrogen as well as the natural gas transported via pipelines need to be compressed before being inserted into the UGS. After a compression step, the gas is ready for injection into UGS through injection wells. The percentage content of gases needs to be determined to avoid overfilling or losses in the reservoir [3].
Loss of containment from the storage reservoir is possible either through the caprock, through discrete fractures or, identified as the most likely, through wells. It is known that the reaction of hydrogen with steel or hydrogen-induced corrosion can cause embrittlement and ultimately premature cracking of well

material [4]. Thus, the hydrogen concentration is needed to be simultaneously monitored and controlled in the whole system.
There are several other issues to be considered which are connected with possible biochemical (sulphate reduction, iron reduction, other microbial processes) or geochemical (abiotic calcification) interaction of hydrogen with material of the reservoir walls or the reservoir content.

Regarding the issues in UGS just mentioned, the research focus in the project in Task 3 was oriented on gas stratification and gas mixing which can have a crucial impact on hydrogen distribution and precision of gas flow rate measurements.

Gravity segregation of a hydrogen + methane mixture

In general, gravity segregation (stratification) of the gases discussed here is possible due to significant differences in their molecule weights. The possibility of gravity segregation is important for determining the efficiency of UGS and how injection or withdrawal can impact the efficiency [5].

However, based on research conducted at the molecular level, the gravity driven segregation of hydrogen and methane seems to be insignificant due to intermolecular attraction and diffusion driven by concentration gradients [6]. These theoretical reasonings were in agreement with experiments [7] as well as with modelling results using molecular dynamic simulations [8] or with our own CFD simulations, see Section 2.2 CFD simulations below.

Hydrogen + methane mixture

The second issue studied in the project was the investigation of the hydrogen-methane mixing process in pipelines. A defined high-quality mixture is demanded in the gas meters to fulfil the requirements for the measurement uncertainty as well as for safety requirements. The lower density from the hydrogen content can potentially lead to hydrogen migration upward to the top of the reservoir and decreasing deliverability. The strongly inhomogeneous distribution of hydrogen also can indicate potential location of wall material degradation [9].

To promote mixing, the passive inflow mixer is often used, as tested, for example, by Kong et al. [10]. However, for cases where that mixing approach cannot be used, the process of mixing was studied for different initial conditions.

2.2 CFD simulations

Several issues have been investigated in previous studies using modelling or simulation techniques. Injection of pure gaseous hydrogen into a natural gas pipeline at a T-junction was simulated using CFD technique in [9]. The influence of branch pipe diameter and pipe orientation is discussed. An analysis of different pipe injections indicates that mixing is best when injected from the bottom so that hydrogen has the potential to rise through the pipe flow.

Numerical simulation of hydrodynamic and gas mixing processes in underground hydrogen storages were done in [11]. Five years of seasonal cyclic operation were simulated to predict injection and production rates, pressure response and composition of the produced stream.

It was observed that the injection of hydrogen leads to a relatively uniform displacement although an effect of gravity segregation was already indicated.

Numerical and analytical models were used to study the hydrodynamics effect influencing the injection of hydrogen and methane for storage into a simplified two-dimensional reservoir in [12]. Stratification of hydrogen + methane mixtures were studied in [13].

2.2.1 Mixing simulations

In our study within the MefHySto project, we focused on simulations of the hydrogen-methane mixing process in a pipe with a length of 40 m and an inner diameter of 0.4 m. The long pipe contained flowing methane and the hydrogen was injected via a joined pipe of the same diameter 0.4 m. The common methane-hydrogen flow rate was 3000 m³/h with an internal pressure of 50 bar. The mixture mass composition was tested for hydrogen to methane ratios of 50:50 and 80:20, respectively.

The structured mesh for simulations was designed according to rules for LES and RANS simulations. The number of cells was up to 10 million for LES attitude. Mesh details are illustrated in **Figure 1** and **Figure 2**.

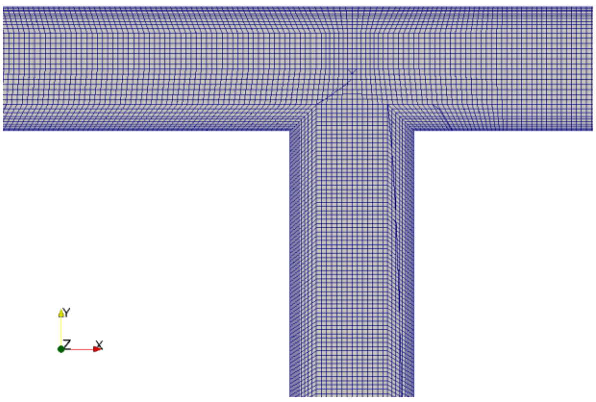

Figure 1: Detail of structured mesh of T-junction in geometry for gas mixing simulations.

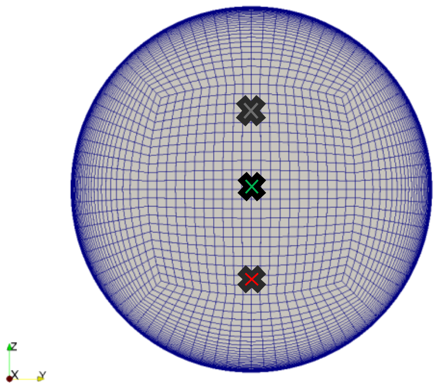

Figure 2: Mesh detail in pipeline cross-section. The location of hydrogen volume fraction evaluation is depicted with a coloured cross.

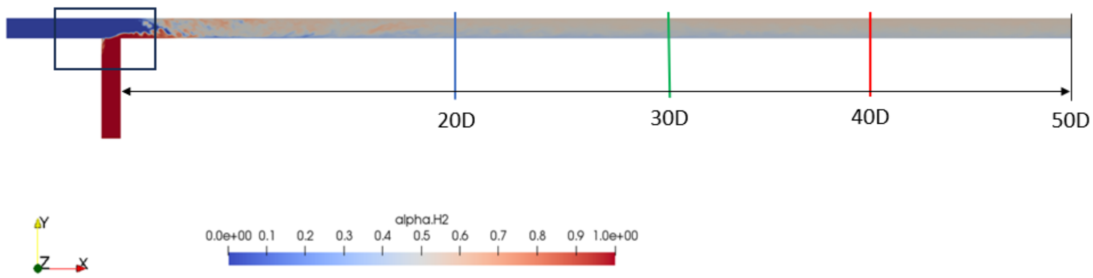

Figure 3: Horizontal pipeline with an inlet pipe for hydrogen inlet. Coloured lines indicate the location of profile evaluation, see Figure .

At first, the hydrogen-methane mixing was studied in a pipe of 40 m length (*L*) and an inner diameter (*D*) of 0.4 m (*L* / *D* = 100), a volume flow rate of 3000 m^3/h for a pressure of 50 bar and in a pipe of 5 m length and an inner diameter of 0.1 m (*L* / *D* = 50), with a flow bulk velocity of 2 m/s and a pressure of 5 bar.

The mixture quality was evaluated using the hydrogen volume fraction both in radial and axial directions. In the axial direction, the volume fraction was read along the central axis of the pipeline and along the axis at 25 % and at 75 % height of the cross-section, as illustrated in **Figure 2**.

In radial direction, the hydrogen volume fraction and velocity profiles were studied at distances of 20D, 30D and 40D from the T-Junction, as illustrated in Figure 3. The corresponding profiles can be seen in Figure 4. The profiles read at 20D, 30D and 40D after the T-junction are marked using blue, green and red colour, respectively. As we can see, the velocity profiles as well as the hydrogen volume fraction profiles are becoming flatter with increasing distance from the T-junction. The difference between hydrogen volume fractions near the bottom and near the top of the pipeline is about 2 % at the distance of 20D and about 1 % at the distance of 40D after T-junction, respectively.

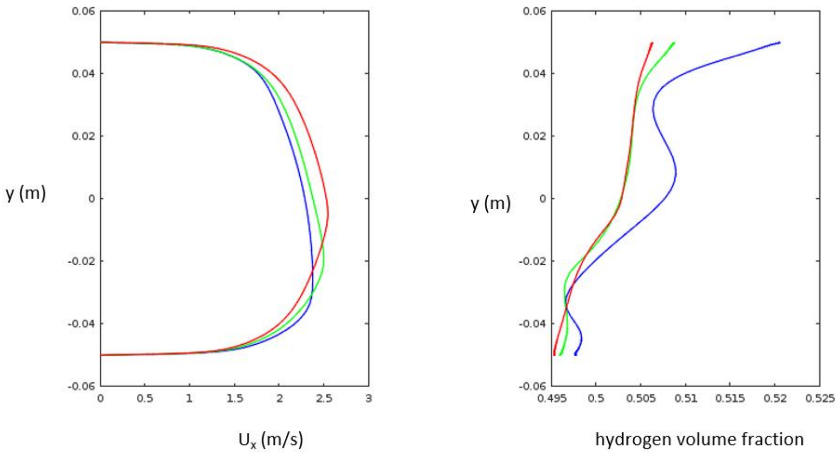

Figure 4: Velocity profiles and hydrogen volume fractions in vertical cross-sections at a distance of 20D (blue), 30D (green) and 40D (red) from T-junction. Simulations were done for a 50D long pipe at a pressure of 5 bar.

The hydrogen volume fraction in streamwise direction is depicted in Figure 5 for the 50:50 and 80:20 initial hydrogen + methane mixture. The hydrogen volume fraction is evaluated at the central axis and at the axis in 25 % and 75 % of the pipeline height as depicted in **Figure 1** from simulations in 50D long pipe at a pressure of 5 bar. The results correspond to the observation in **Figure** , that the mixture quality is already better than 99 % at the distance about 30D and further from T-junction for an initial 50:50 mixture. In case of an 80:20 initial mixture, the mixing process shows higher disturbances in concentration. However, at the distance 50D from T-junction the mixing is even better than in case of 50:50 initial mixture.

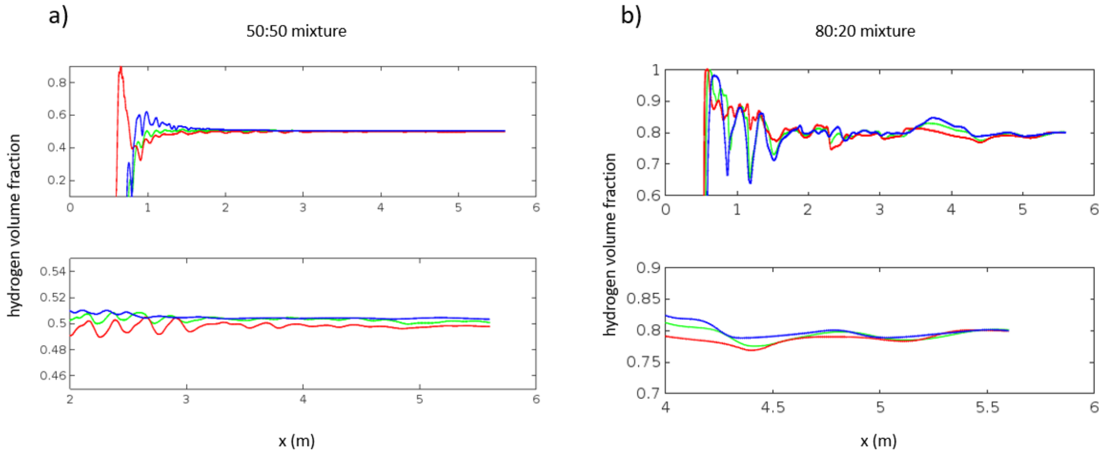

Figure 1: Hydrogen volume fraction in streamwise direction at central axis of the pipeline (green colour) and at 25% (red) and 75% (blue) height of the pipeline. Simulations were done for the 50D long pipe at a pressure of 5 bar for a) the 50:50 initial hydrogen + methane mixture and b) the 80:20 mixture.

2.2.2 Stratification simulations

Gravity segregation in the pipe was simulated using results from the previous paragraph. The pipeline filled with non-uniformly distributed hydrogen had been closed and a new transient simulation was performed with zero flow rate of gases. It was observed that, due to the diffusion process, the hydrogen is very well distributed in the entire inner space of the pipe and no stratification was observed within a time frame of 2000 s. This is corresponding to theoretical findings and agrees with the statement that gravity segregation is not significant for a hydrogen + methane mixture in reasonable dimensions and time frame.

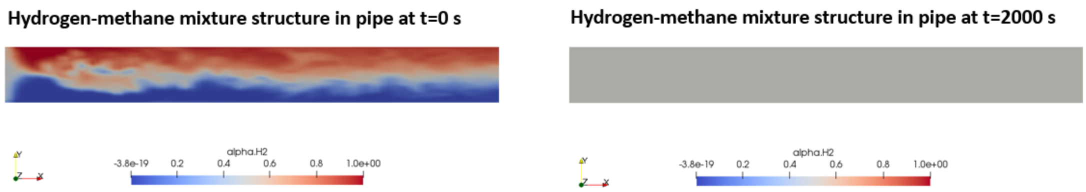

Figure 6: Uniform results for a hydrogen + methane mixture from simulation after a time period of 2000 s.

2.2.3 Conclusions following from CFD simulations

Hydrogen mixing is highly dependent on turbulence effects. As well as the velocity profile becomes flat with increasing distance from the pipe inlet, the mixture is becoming uniformly distributed with increasing pipe length downstream hydrogen injection point. Next to the pipe length, the induced turbulence intensification (e.g. by employed T-junction) accelerates the gas mixing. The quality of the mixture defined as difference of the hydrogen volume fraction sampled at 25% and 75% height of the cross-section shows quick mixing in downstream direction. The mixture quality is a better than 99 % at the distance about 30D and further from T-junction for an initial 50:50 mixture. In case of an 80:20 initial mixture, the mixing process shows higher disturbances in concentration, however, at the distance 50D from T-junction the mixing is even better than in case of 50:50 initial mixture.

From several simulations as well as from literature review follows, that the mixing induced by diffusion is strong enough to prevent stratification even if the flow is stopped. In case of a zero-flow rate, buoyancy effects and diffusion support mixing and lead to a uniformly distributed hydrogen in significant time frame. Stratification was not observed in the simulations done so far.

2.3 Solubility simulations

The solubility of various hydrocarbons in hydrogen and other gases was simulated using thermodynamic programs.

The solubilities of hydrocarbons in hydrogen were simulated using the thermodynamic models of Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK). These thermodynamic calculations are integrated in various programmes (e.g. in the ProII software package) and are based on the thermodynamic data determined by measurement.

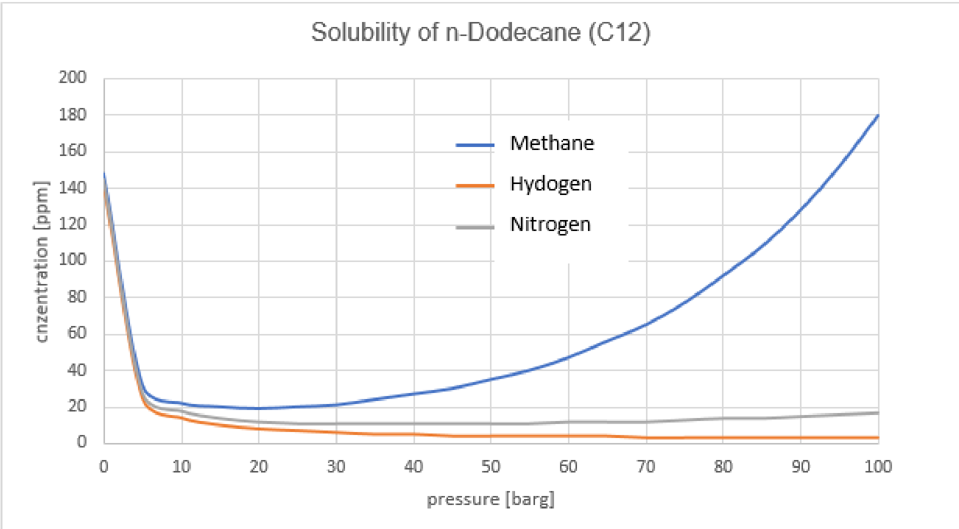

Figure 2: Simulation of the solubility of n-dodecane in different gases.

It was investigated whether thermodynamic data on the solubility of hydrocarbons from C 5 in hydrogen are available or only simulation, e.g. on the basis of Henry's Law. Measurement data do not exist. The reason for this is the extreme metrological effort required to determine this data. Especially at high pressures (>30 bar) and temperatures, no analytical confirmations are available.

The evaluation of the simulations means that the results from these simulations should be viewed critically because thermodynamic data on the solubility of hydrocarbons in hydrogen are still lacking. These data are desired since solubility of hydrocarbons in depleted gas fields is relevant. Such depleted gas fields are used as UGS.

On finding from the simulation results can be viewed as promising, as the effect of a greater solubility of the components is eliminated at higher pressure (except for methane). The effect of retrograde condensation in natural gas leads to condensation of hydrocarbons in the pipeline system. If the real solubility curve would resemble that behaviour as calculated in Figure 7, condensate would not be formed when the pressure was reduced. However, whether this is actually the case remains to be subject of further investigations.

3 Summary

3.1 Summary WP 5

The PFD simulation shows that no stratification could be simulated when injecting Hydrogen into natural gas. Installations for faster mixing of mixtures are recommended.

The following illustration shows the planning of a measuring section for a clean gas. The measuring section is relatively short within a container without special mixing installations.. In many cases, there is not enough space available, so that the question of a mixing section for gases analyzed here is very relevant.

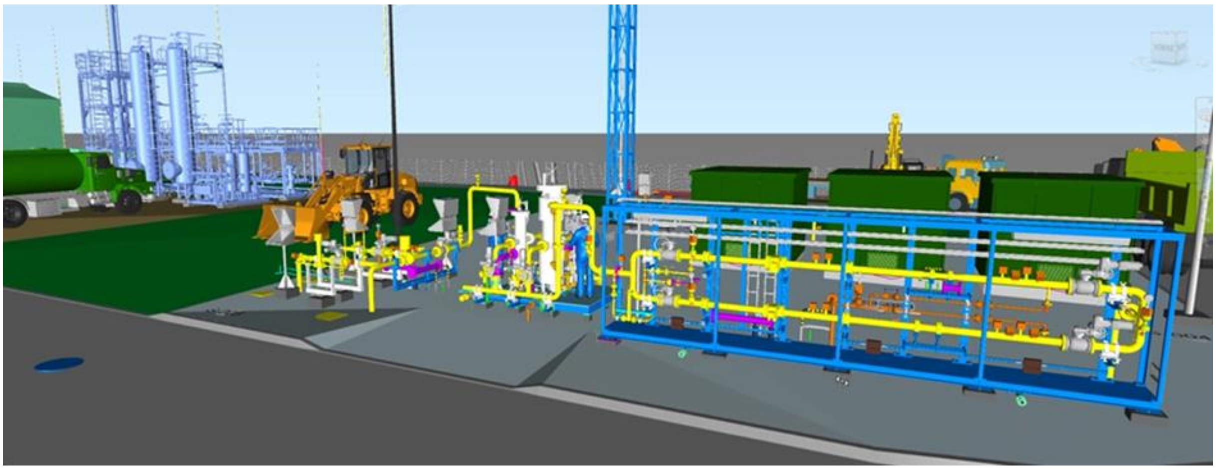

Figure 8: Example for a measuring track (source DBI)

There is a lack of measurement data for exact solubility calculations. Such data were determined for water in the MefHySto project. There is a lack of such data for hydrocarbons, although they are extremely relevant for storage and H_2 transport.

3.2 Recommendations for further investigations

For this part of the investigations, projects arose during the course of the project in which the metrological questions investigated are relevant. Reference is made here to the IPCEI project of NAFTA (Sk). This project is investigating how a former natural gas reservoir can be converted to hydrogen. A mixed gas is extracted from the reservoir, the composition of which varies. Using membrane and adsorption processes, the gases are separated and then utilized separately or mixed together again in a defined manner. This effort is necessary because users of the gas can only work with a constant gas composition. This results in the need to measure quantities and gas compositions correctly (or with variable accuracy) several times.

At the same time, the mixing behaviour of the gases is simulated in these projects. The comparison of the thermodynamic models reveals differences in the dissolution and mixing behaviour. This is due to uncertain or missing data on the solubility of higher hydrocarbons in H2 and methane as a function of temperature and pressure. There is a need for research here.

The project implemented initial steps to record and check requirements and options for measuring relevant parameters at underground gas storage facilities. Approaches to solutions were found that require expansion in further stages.

The following necessary points for further investigation are seen:

- Expansion of the measurement base
- Creation of the thermodynamic basis regarding the solubility of other components (e.g. glycols) in Hydrogen in the relevant pressure range.
- Proof of the possibilities of measuring higher hydrocarbons

Particular reference should be made to the lack of thermodynamic data regarding the solubility of hydrocarbons. This data is important when converting underground gas storage based on exhausted gas or oil fields.

4 Literature

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