Recovery and purification of seasonally stored, high-pressure, green hydrogen from depleted natural gas reservoirs

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Introduction

The research is aimed to support the seasonal storage and withdrawal of hydrogen from a depleted natural gas reservoir. The goal is to minimize repressurization to reduce financial and energy costs. A high-pressure PSA (Pressure Swing Adsorption) unit is employed for this purpose. The main challenge is designing equipment and processes that can produce high purity and recovery even with varying feedstock conditions, which is uncommon for PSA separation. Such conditions depend on the reservoir used. Underground storages require a certain amount of cushion gas, limiting the feedstock's pressure range. Content of the cushion gas, geochemical microbiological interactions as well as mixing effects determine the composition. Field tests are required for the exact development of gas mixture composition through withdrawal. The goal is to set up a framework for the equipment and process design for changing feedstock conditions. In the process under investigation, the pressure can range between 30-70 bar with 65-100 % hydrogen content. The key findings are transferred to a pilot sized plant which will operate as a technological demonstration for high-pressure hydrogen recovery and purification.

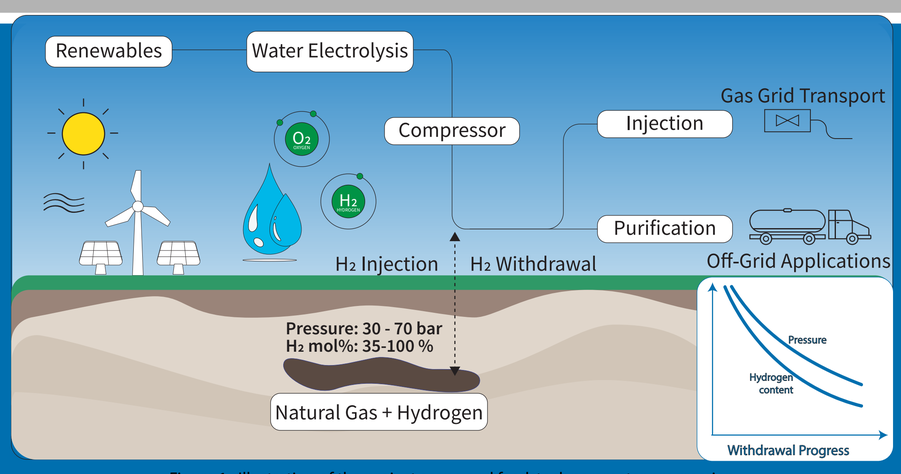

Figure 1: Illustration of the project scope and feedstock parameter progression

Methods

A laboratory-scale pressure swing adsorption unit was designed and built, operational up to 100 bar. The main component of natural gas is methane, and as first approach, binary hydrogen-methane mixtures were investigated, using a commercial activated carbon for separation. An infrared sensor was used to measure methane content in the permeate. Breakthrough, desorption and purging experiments were conducted with four different pressure-composition combinations (modelling different stages of withdrawal) to explore the effects on breakthrough time and find optimal cycle times, blowdown pressures and purge-to-feed ratios. The measurements are also used to verify a process simulation model to allow extending the investigation to all pressure-compostition combinations which might occur as withdrawal progresses. A 12-step purification process was designed for each of the four predetermined combinations. Cyclic measurement were conducted and hydrogen product purity and recovery was calculated.

Table 1: Definition of withdrawal stages

	Pressure	H_2 mol%
Stage 1	60 bar	98 %
Stage 2	50 bar	90 %
Stage 3	35 bar	80 %
Stage 4	25 bar	70 %

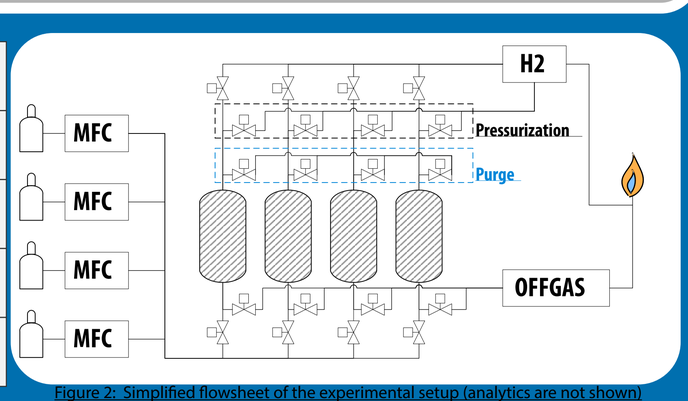

Figure 2: Simplified flowsheet of the experimental setup (analytics are not shown)

Table 2: Layout of the 12-step pressure-swing separation process

STEP #	1	2	3	4	5	6	7	8	9	10	11	12
Col1	AD1	AD2	AD3	EQ1DN	PPG	EQ2DN	BD	PG	EQ1UP	EQ2UP	PR1	PR2
Col2	BD	PG	EQ1UP	EQ2UP	PR1	PR2	AD1	AD2	AD3	EQ1DN	PPG	EQ2DN
Col3	EQ1DN	PPG	EQ2DN	BD	PG	EQ1UP	EQ2UP	PR1	PR2	AD1	AD2	AD3
Col4	EQ2UP	PR1	PR2	AD1	AD2	AD3	EQ1DN	PPG	EQ2DN	BD	PG	EQ1UP

Results

Breakthrough occured between 1260 and 490 seconds, depending on feed composition and pressure. This results in a 2.5-time difference between the start and end of withdrawal. Decreasing adsorption pressure resulted in lower maximum blowdown pressure, and shorter purging times required. In the separation experiments the pressure values were close to ideal. The only consistent, significant pressure loss was noticed in the adsorption step when pressurization took place on another column. This effect can easily be mitigated with the installation of an extra valve. Hydrogen purity - calculated from mass balance - was above 99.90% and no major methane breakthroughs were recorded. Recovery (product-to-feed hydrogen ratio) ranged between 49% and 81% throughout experiments and showed a decreasing trend as theroetical withdrawal progressed.

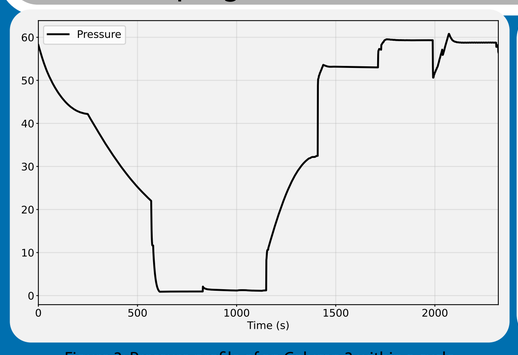

Figure 3: Pressure profile of an Column 3 within a cycle

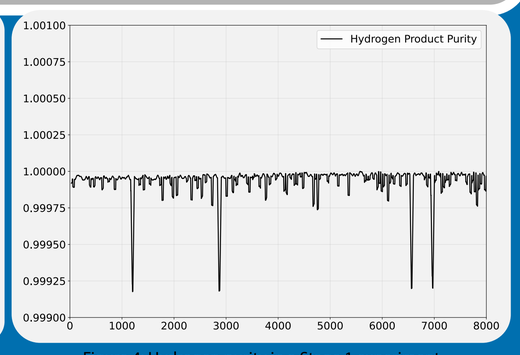

Figure 4: Hydrogen purity in a Stage 1 experiment

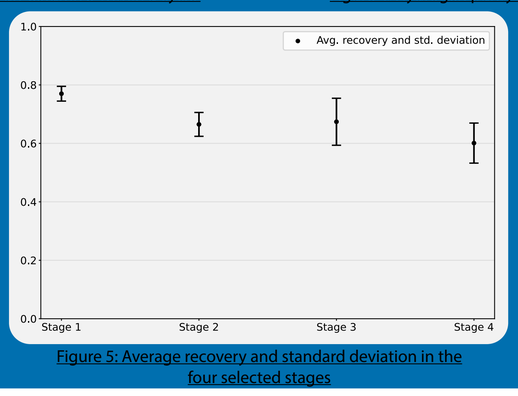

Figure 5: Average recovery and standard deviation in the four selected stages

Conclusions

Laboratory experiments demonstrated that pressure swing adsorption (PSA) is suitable for high-pressure hydrogen purification. Product pressure can be kept as high as to directly inject into the gas grid, eliminating the need of product recompression. High product purity can be reached, allowing the direct use of purified hydrogen, even in fuel cells to generate electric power. Furthermore, reasonable average hydrogen recovery (60-80%) was achieved. State of the art industrial systems operate with ca. 80% recovery with fixed feedstock conditions. The investigated separation process is a promising candidate for cost-effective, on-demand hydrogen recovery and purification from natural gas reservoirs. It can be a key technology in the seasonal storage of renewable energy. Further research is necessary, namely, separation from multicomponent mixtures (i.e. natural gas), upscaling and construction of a flexible control strategy.

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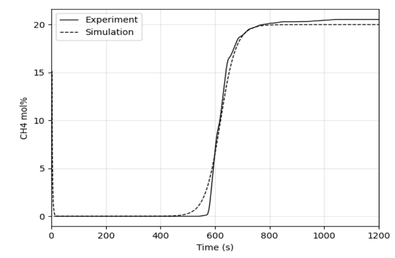

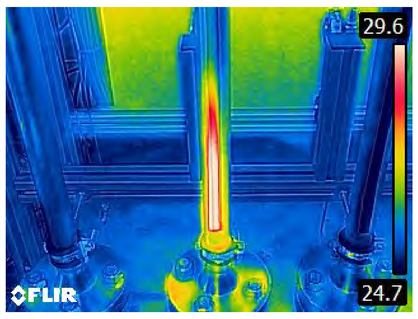

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