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A new cryogenic high-pressure H_2 test area: First results

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ABSTRACT

An innovative hydrogen test area for cryogenic high-pressure applications has been put into operation at the ILK Dresden. This test area allows fundamental investigations on hydrogen (in all its phase states) and on gaseous helium. Furthermore, tests and qualification of components of any kind in the temperature range from room temperature down to 10 K and under pressure conditions ranging from high vacuum to 1000 bar are possible. In the framework of a research project, investigations of the charging and discharging process of hydrogen tanks, and the development of new storage technologies to achieve a high hydrogen storage density up to 100 kg/m³ are feasible. Our experiments promote the intricate developments of new components in relation to the handling of supercritical mediums. Thereby, experiments on re-cooling systems in form of capillary expander or Joule-Thomson-cooler are performed as well as on special latent-heat storage systems based on eutectic mixtures. The current status of the development up to test set-ups and experimental results is presented. Furthermore, results of numerical calculations are shown regarding the optimization of process control.

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1. INTRODUCTION

1.1. Hydrogen test areas

Hydrogen storage has become a field of rising interest in recent years due to its high capability for solving problems connected with non-continuous energy generation. Up to now, hydrogen test areas are often focussed on special experiments in pressure and temperature regimes. Therefore, fundamental results and scientific findings are still limited.

1.2. State of the Art of Hydrogen Storage

Numerous studies on hydrogen storage are focused on liquid hydrogen. However, liquid hydrogen requires cryogenic storage since it boils at about 20 K (under ambient pressure). Hence the storage vessels must be well insulated to prevent significant boil-off. For instance BMW has been working on a liquid tank for cars, producing for example the BMW Hydrogen 7 [1]. In another method, compressed hydrogen is stored in vessels up to 700 bar at room temperature used for mobile storage in hydrogen vehicles such as applied by Honda, Nissan, Toyota, or Mercedes [2, 3]. Both methods can be considered as an approach to enhance the specific energy in mobile applications.

1.3. Project Innovation

Calculations based on thermodynamic data [4] have shown that the density of hydrogen can be considerably increased by storing it in the supercritical state, *i.e.* above its critical point. So, in the following we present experimental setups for hydrogen storage in such a state. For that we have built up a new test area which enables investigations in the pressure range up to 1000 bar and down to cryogenic temperatures. The project includes also studies on additional components like re-cooling technologies and latent-heat storage systems in order to improve the performance of a combined hydrogen storage system. This kind of hydrogen storage was patented [5].

Supercritical storage is not limited to the case of hydrogen. For instance, in the case of methane, numerical simulations have revealed a storage density which is more than double at 220 K (supercritical state) compared to storage at room temperature under otherwise equivalent pressure (around 150 bar). In our experiments storing natural gas under the above conditions resulted in an increase of density by a factor of 2.2. Thus, supercritical storage is a very promising way to enhanced storage densities.

2. BASICS OF PROJECT

2.1. Hydrogen Phase Diagram

The phase boundaries of hydrogen are shown in Figure 1. The values for the transitions between solid, liquid and gaseous phases have been calculated [4]. Above the critical point (T_{crit} = 33.2 K, p_{crit} = 13.15 bar) the supercritical state (*i.e.* gas of high density) exists. At temperatures near but below the critical point, the liquid shows enhanced compressibility.

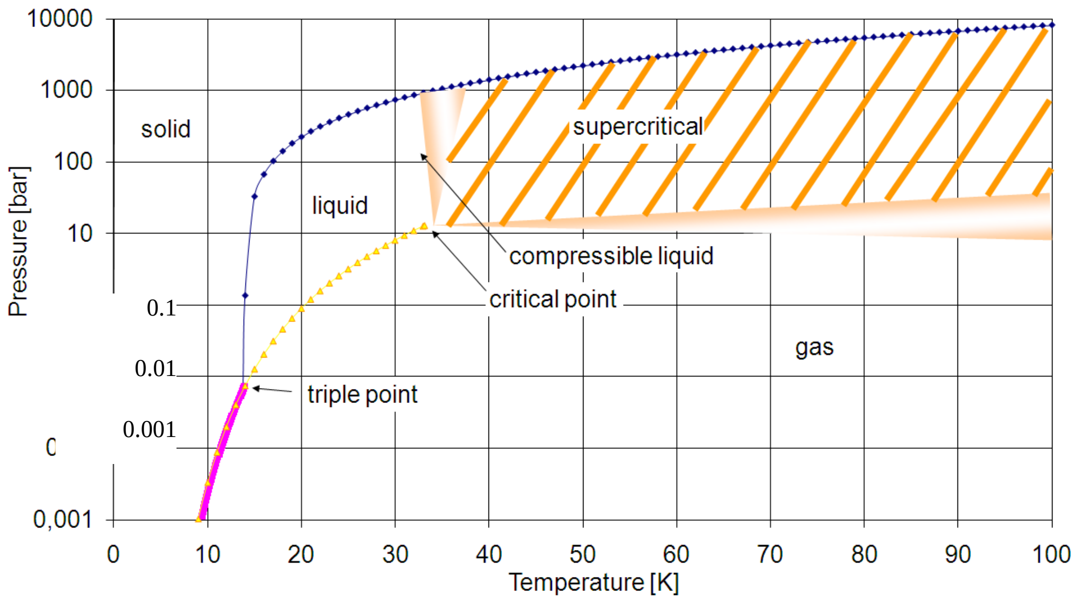

Figure 1. Phase diagram for hydrogen. The symbols correspond to numerical results [4]. Further transitions are shown schematically. The hatched area indicates the supercritical range (i.e. fluid of high density).

2.2. Cryogenic High-Pressure Hydrogen Storage

Figure 2 shows the hydrogen density depending on temperature and pressure. In general, the stored density rises with increasing pressure and decreasing temperature. Most pronounced changes are observed near the critical point. Well below T_{crit}, an increasing pressure does not enhance the density significantly due to the nearly "incompressible" liquid state.

The established storage concepts mentioned above, i.e., those in the liquid state around 20 K and in the gas state within the pressure range between 250 and 700 bar at room temperature, result in a stored density of approximately 70 kg/m^3 (liquid) and up to 40 kg/m^3 (gas), respectively. The advantages of supercritical storage (the target of the storage parameters of the ILK Dresden is between 500 to 1000 bar at $T_{crit} \leq T \leq 75$ K) are evidently: An increased density of up to 100 kg/m^3 and more is possible for temperatures well above those of the liquid storage thus reducing the cryogenic requirements and hydrogen losses. The latter is due to a lower boil-off which results from a higher maximum pressure compared with the liquid-storage parameters.

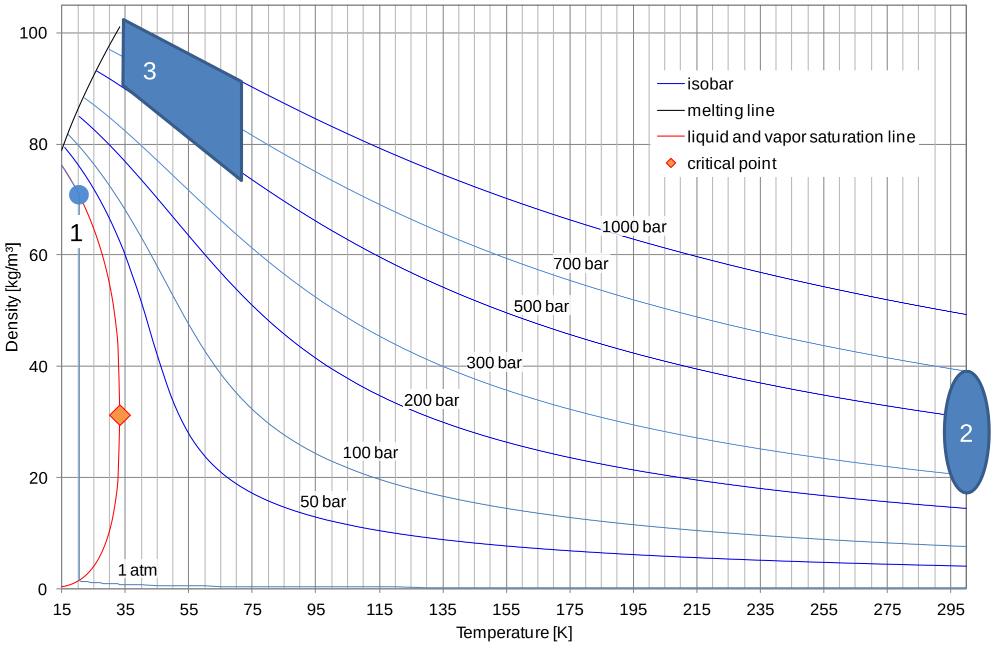

Figure 2. Shown is the hydrogen density as function of temperature at different pressures (lines). Highlighted areas mark state-of-the-art results: (1) liquid around 20 K, (2) pressurised gas around 300 K, and (3) cryogenic compressed gas, the project target of the ILK Dresden.

3. THE HYDROGEN TEST AREA OF THE ILK DRESDEN

Within the last two years, the hydrogen laboratory at the ILK Dresden has been designed and built. Some of its main components are shown in Figure 3. A high-pressure compressor enables the use of gases in the range up to 1000 bar. Minimum temperatures down to 10 K are achieved by a Gifford-McMahon cryocooler. Noteworthy, the gas supply also allows the utilisation of helium instead of hydrogen not only for inertisation but also for additional experiments in the mentioned range of pressure and temperature. Thus, a comparison of results on hydrogen with the properties of an inert gas is possible.

Figure 3. Some components of the hydrogen test area at the ILK Dresden: e.g. (1) – high-pressure compressor, (2) – dewar of the cryo¬cooler, (3) – gas supply for hydrogen and helium, (4) and (5) – mass flow controller.

An overview of the hydrogen flow realized in the test area is given in Figure 4. The main components mentioned above are accompanied by a number of measuring instruments for mass flow, pressure, temperature, and safety equipment. The latter are connected with the exhaust line in order to establish a safe state in case of critical operation.

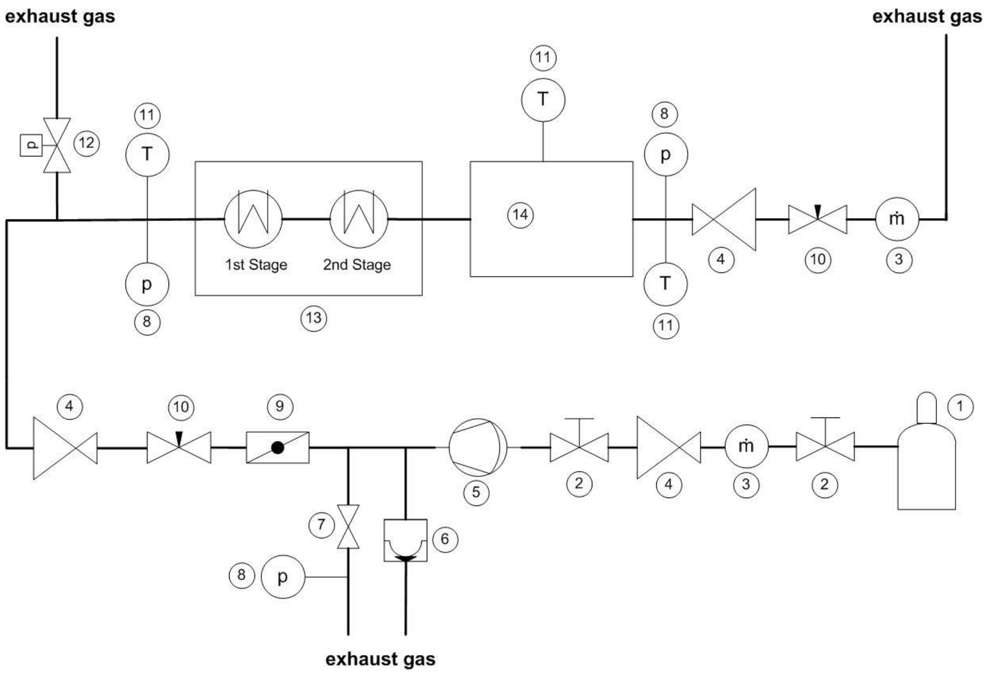

Figure 4. Schematic structure of the components within the main part of the hydrogen test area: (1) – H_2-source, (2) – lock valve, (3) – mass flow meter, (4) – pressure reducer, (5) – high-pressure compressor, (6) – rupture disc, (7) – safety valve, (8) – manometer, (9) – back-pressure valve, (10) – needle valve, (11) – thermometer, (12) – pneumatic valve, (13) – cryocooler, (14) – experiment (storage tank and additional components).

4. EXPERIMENTS

4.1. First Tests with Hydrogen

Within one of the first tests of the cryogenic high-pressure hydrogen test area, the melting line has been verified for a large pressure range. A typical pressure development is shown in Figure 5. A comparison between measured values and theoretical data is shown in Figure 6. Depending on temperature, the evolution of a pressure drop between inlet and outlet of the vessel clearly indicates the presence of a solid phase. The measurement gives reasonable agreement with the known phase diagram.

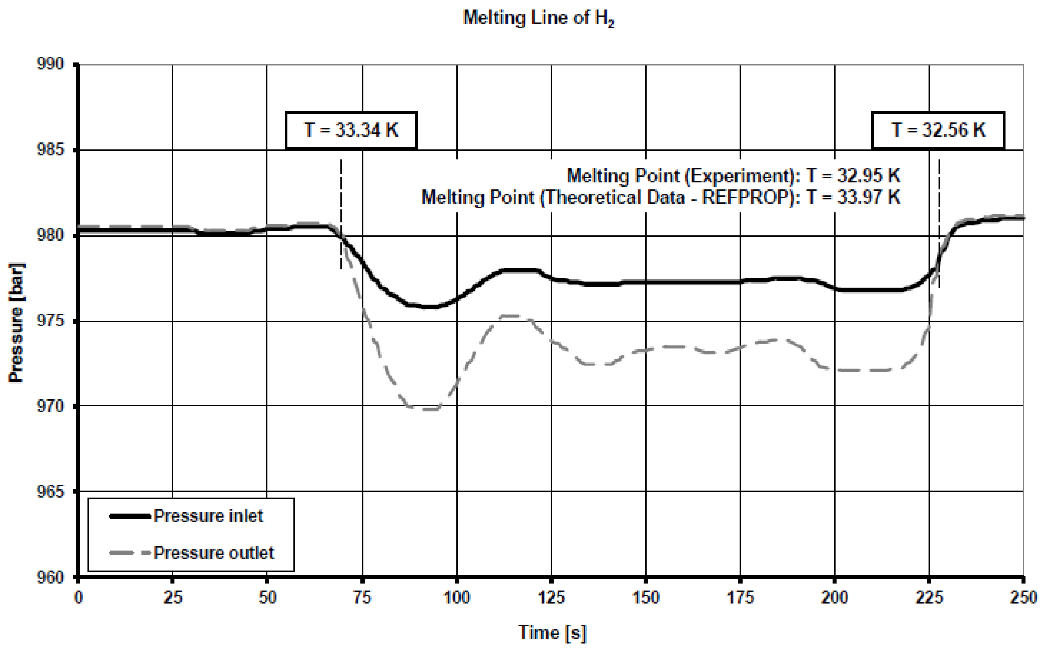

Figure 5. Typical pressure development at the melting point (temperature is varied; see text).

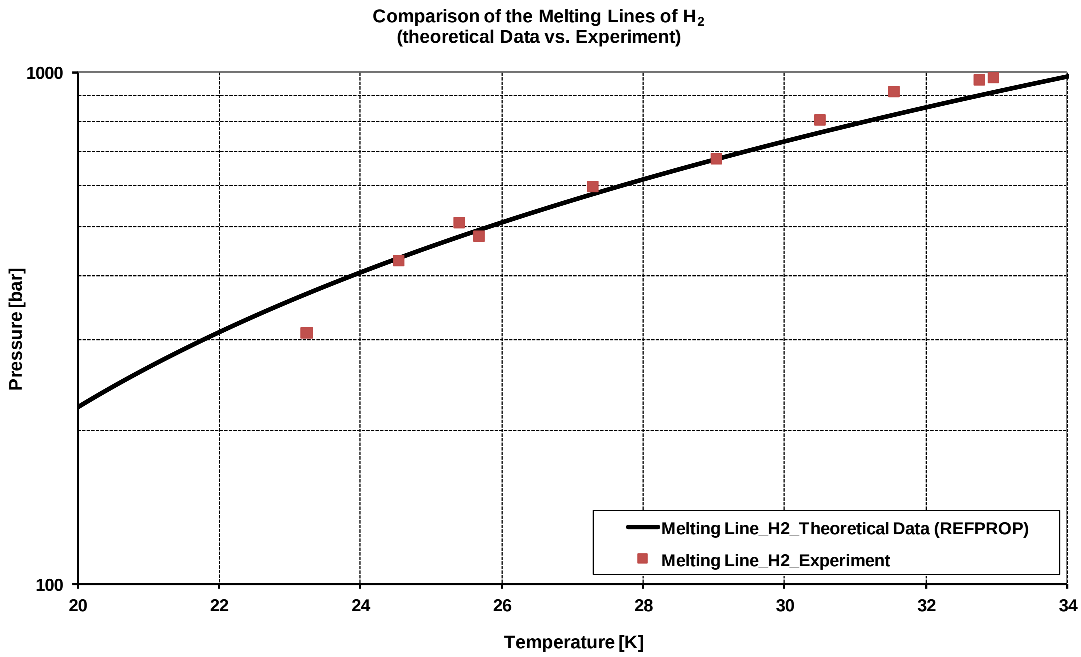

Figure 6. Comparison between measured values (squares) and theoretical data (thick line; [4]) for the melting line of hydrogen.

4.2. Latent-heat Storage

Due to a permanent heat flux into the hydrogen reservoir, a latent-heat storage system is used to guarantee a required storage temperature for a certain time. To develop and investigate such a storage system for these low-temperature conditions, an additional test area for material characterization has been built up, shown in Figure 7.

Interesting materials for latent-heat storages are typically eutectic mixtures of members of the alkane series as e.g. methane, ethane, and propane as well as a fraction of nitrogen. The measured solidification temperature of the tested mixtures is between 63 K and 65 K with a corresponding theoretical transformation-enthalpy of approximately 65 kJ/kg [6]. For example, the measured value for methane is 89.3 K with a latent heat of fusion of 59.2 kJ/kg which is in good agreement with literature data [6]. Currently a suitable latent-heat storage device for the integration in the whole hydrogen test area is under construction. In the final setup, the hydrocarbons will be stored in a separate vessel to serve as a working material but not as a material under test.

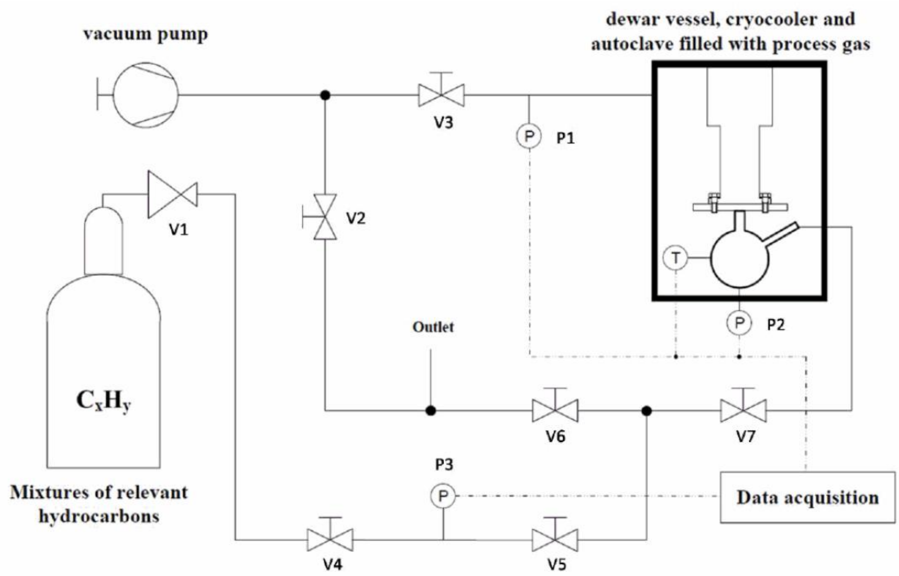

Figure 7. Schematic structure of the experimental station for material characterization

4.3. Re-cooler

First successful tests of a re-cooler have been performed using a separate experimental setup suited for gaseous nitrogen and gaseous neon. Nitrogen gas is taken from a standard gas cylinder. Its pressure is reduced to values of typically 5 bar. A pre-conditioner is used to assure defined and stable temperatures of the gas prior entering the cooler. In order to determine the cooling power, the cooler is kept at constant temperature by a heater whose power is measured. The data for pressure, temperature, heating power, and volume flow is collected and recorded. The measured cooling power was in agreement with calculated values. As expected, the best theoretical approximation of the measurement data can be obtained by use of a model considering both, the Bernoulli effect and the Joule-Thomson effect.
The next experiments will be performed with hydrogen within high-pressure H_2 test area.

5. CONCLUSIONS

A hydrogen test area for cryogenic high-pressure applications has been built up and tested. First experiments within the new H_2 test area show good results not only on the handling of cryogenic gases and liquids but also on potential benefits from additional components like re-cooling and latent-heat storage systems. Experiments on components like an integrated latent-heat store are on progress. A promising way of a high density hydrogen storage is described and patented [5]. Experimental investigations on the theoretically expected enhanced storage density in the supercritical state are currently performed.

6. REFERENCES

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