Hydrogen

Metrology for sustainable hydrogen energy applications

EMPIR Grant Agreement number: 15NRM03 Hydrogen

Project short name: HYDROGEN

WP3: Development and validation of traceable methods for mass measurements of hydrogen absorbed in metal hydrides

Task 3.2: Validation of a traceable method for the measurement of hydrogen mass absorbed in metal hydrides storage tanks

Deliverable D5 (Validation Report)

Development of a traceable method for measuring the hydrogen mass absorbed in storage tanks (hydrides AB, AB2 and AB5)

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Table of content

1 Introduction

1.1 Summary of the EMPIR project 15NRM03 "Hydrogen"

This project addresses the standardisation priorities required in the Directive 2014/94/EU on the deployment of Alternative Fuels Infrastructure through the development of metrological methods and measurement techniques needed to enable the safe introduction of hydrogen in the energy sector for mobile applications.

1.2 Summary of WP3 "Development and validation of traceable methods for mass measurements of hydrogen absorbed in metal hydrides"

The aim of this work package (WP) is devoted to the development of a consistent method to assess the absorbed mass (or volume) of hydrogen in a reversible hydride tank. Hydrogen storage by reversible hydride metal is more and more used in various storage systems. However, this storage method does not provide one-to-one relationship between absorbed mass of hydrogen, pressure and temperature. The knowledge of observed physical variables such as pressure and temperature are not sufficient to assess the residual hydrogen contained in the tank.

The ISO 16111 standard Transportable gas storage devices – Hydrogen absorbed in reversible metal hydride is the standard devoted to this type of tank. ISO/TC 197/WG 25 is working on a revision of this standard. Particularly, issues arise as the standard states that a hydrogen cycling test has to be performed during qualification test and that the tank shall be cycled when charged with hydrogen, from not more than 5 % of rated capacity to not less than 95 % of rated capacity. ISO 16111 does not currently recommend the use of any specific measurement technique or method with respect to the cycle test. The results of WP3 will give proposals for accurate measurement methods of the hydrogen residues associated to uncertainties.

1.3 Scope of work in WP3

In WP3 the partner MAHYTEC has provided, in each case, an AB5 and AB tank to two other project partners FHA and CEA-Liten. The tanks contain of 100 g hydride (about 1.5 g of H_2 absorbed) and have a total weight of 650 - 700 g. The tanks were supplied with a valve and a self-sealing nozzle.

There are mainly two methods for the determination of the volume stored into the tanks; mass measurement (weighing method) and flow measurements method. The focus in this WP was on the second, the flow measurement method.

Each partner was free to develop and use its own measurement method. The goal is to compare the measurement results (accuracy, reproducibility) with different methods for the same tank. The main difficulty is the very high difference between the mass of the tank and the small mass of the stored hydrogen. In WP3 an eye was kept on the measure of equilibrium pressure and hydrogen flow according to the heat for the volume or mass measurements.

In WP3 mainly two approaches concerning the flow measurement method were investigated. FHA designed a test rig based on a combination of mass flow meters and needle valves and CEA-Liten built-up a test rig primary consisting of a single mass flow controller. Both approaches will be described in more detail in the following report.

2 MAHYTEC – Innovative Energy Solutions

Based in Dole in the Franche-Comté region, MAHYTEC is an innovative company, on hand to listen and provide solutions to your needs in energy storage.

Started by four co-founders specialized in materials science, MAHYTEC now employs over 20 employees offering a wide range of skills. MAHYTEC relies on a solid experience and a proven know-how to offer a customized approach to the most complex problematic in the fields of energy and materials mechanical behaviour. MAHYTEC helps its customer to design their structure and optimize their mechanical and energetic performances.

MAHYTEC will only provide the metal hydride tanks (type AB5) for the measurements. The actual measurements will be performed by the project partners FHA and CEA-Liten. Since MAHYTEC has performed some measurements related to this task, selected results are presented in this report.

2.1 Fundamentals

Pressure-Compression-Isotherm

Intermetallics are able of absorbing hydrogen and then undergoing a phase transformation that gives the PCI (Pressure-Composition-Isotherm) equilibrium, a three-phase characteristic at a given temperature.

The first step sees an increase in the pressure correlated with the increase of the hydrogen content present in the intermetallic, the second corresponds to the stabilization of the pressure during the phase transformation, the reorganization of the mesh of the intermetallic and positioning of the hydrogen atoms in interstitial spaces. Finally, after saturation, a further increase in pressure occurs.

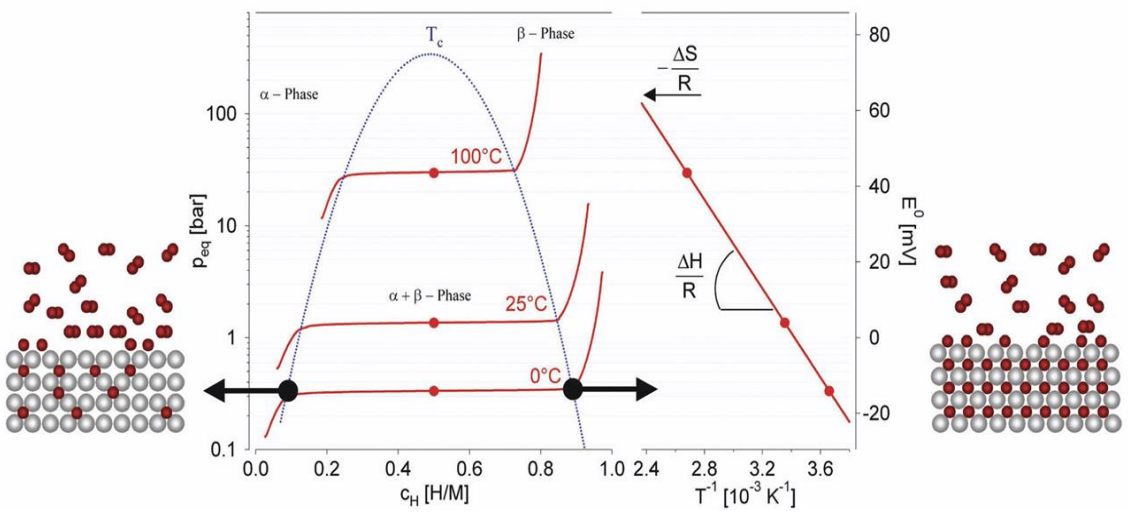

Figure 1 – Diagram of typical PCI.

The experimentally constructing the PCI curves consist to finding the correspondence between the equilibrium pressure P_{eq} and the quantity of hydrogen absorbed n for one temperature T. Measurements are made from equilibrium point to equilibrium point.

Obtaining this curve is very useful because it enables to know at a given temperature the hydrogen absorption capacity of a hydride according to its pressure in absolute bar (bara). It provides an initial estimation on their performance and subsequently enables to eliminate hydrides with poor performances without having to do expensive compression tests, or to be able to optimize them according to the desired parameters.

2.2 Manufacturing of the hydride tanks

A hydride tank is composed by a pressure shell in aluminium which holds the pressure and a hydride which absorbs the hydrogen. MAHYTEC is developing these two parts.

2.2.1 Cutting material and cleaning

Knowing the proportion of each element, the raw materials have to be cut in order to get the right mass. Then, they are arranged in the crucible. Taking into account the fact that we use an induction furnace for fusion, we must use long and non-powdery materials so that the magnetic field can operate.

2.2.2 Fusion and cooling

The intermetallic materials chosen are produced by melting the different pure elements in an induction furnace with a maximum capacity of 5 kg. The raw material, once prepared, is placed in a crucible.

Figure 2 – Picture of the material in a crucible at MAHYTEC.

The oven is then closed. A step of emptying and scavenging with neutral gas is carried out before applying the electric field necessary for the fusion of the various elements. It is now possible to melt the whole elements at a temperature between 1500 and 1800 °C; it is recommend heating it until it is "bubbling" in order to have a good homogeneity of the elements. After, the intermetallic materials are casted in a mould.

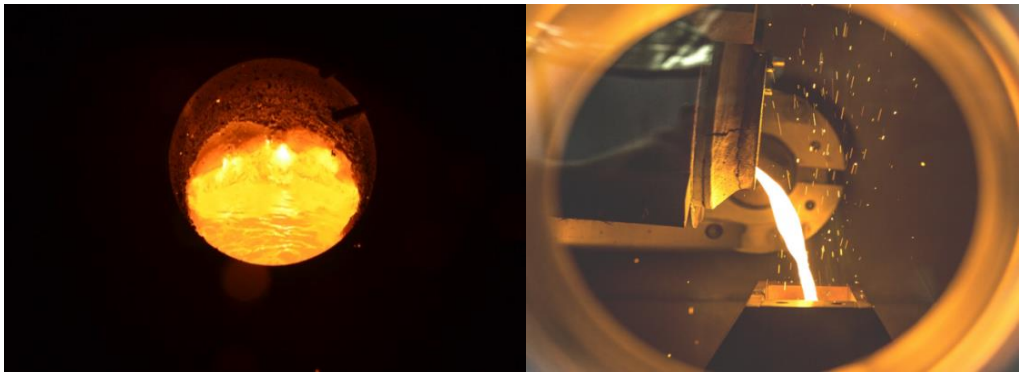

Figure 3 – Fusion of pure elements at MAHYTEC.

After the good hydride ingot is obtained it must be cooled in vacuum and with neutral gas. Finally, the furnace is opened to unmould the ingot which is now at a low temperature.

Figure 4 – Hydride ingot after cooling and demoulding at MAHYTEC.

The ingot is reduced in powder and inserted into the tank.

2.3 Conception of the AB5 and AB tanks

To design a tank, several parameters have to be considered:

- The hydrogen capacity to store which gives the internal volume,
- The length-diameter ratio for the sizing of the tank,
- The calculation of the thickness for the resistance to pressure,
- The choice of material (H_2 compatibility, corrosion, mechanical resistance, thermal conduction coefficient),
- Filtration to contain the hydride inside the tank
- The type of connection (thread, withstand to pressure, ...),
- The nature of the seals (compatibility H_2, temperature of use, extrusion, ...),
- The weight,
- Security system integration,
- The need for a heat exchanger,
- ...

As part of the EMPIR project, MAHYTEC realized a tank designed only for tests:

1) which respects the previous points (H_2 compatibility, pressure resistance, ...),
2) which is light enough to be weighted with a precision scale,
3) which can store 100 g of hydride,
4) which can fit a standard heating collar (diameter 60 mm)?

A shut-off valve and a self-closing fitting are installed on the tank to facilitate the connection. To validate the conception, we realize a pressure simulation of input of tank.

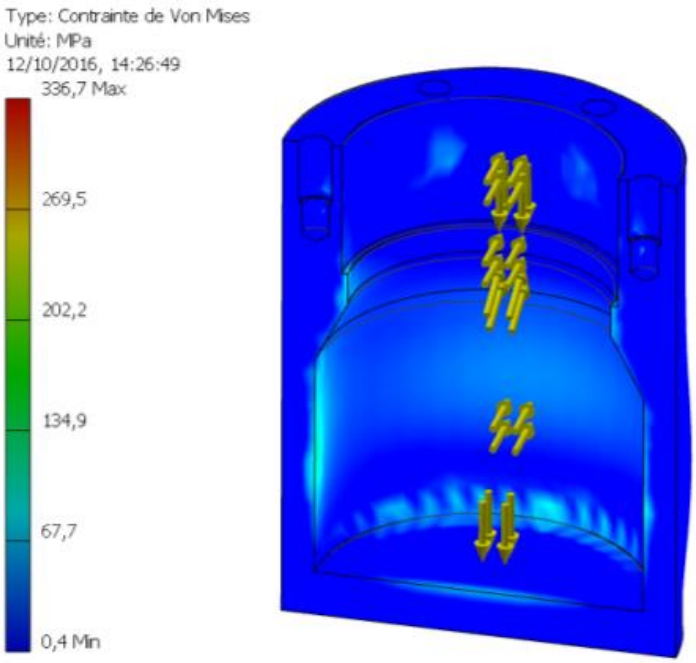

Figure 5 – Diagram of typical PCI.

The main characteristics of the AB5 and AB tanks are described below.

MASS TOTAL OF TANK, VALVE AND HYDRIDE	710 g
MASS OF HYDRIDE	100 g
MASS OF HYDROGEN STORED	1.5 g
OPERATING TEMPERATURE	5 to 45 °C
STORAGE TEMPERATURE	-10 to 65°C
MAXIMUM PRESSURE	75 bar
MAXIMUM REFILLING PRESSURE	15 bar
ABSOLUTE WORKING PRESSURE AT 22°C	2.5 bar (± 0.5 bar) AB5 2.2 bar (± 0.5 bar) AB
HYDRIDE TYPE	AB5 and AB
STATE OF HYDRIDE	ACTIVATE
ACTIVATION OF HYDRIDE	11/11/2016 AB5 01/03/2018 AB

Figure 6 – Characteristic of hydride tank (AB5 and AB type).

Once the tanks are assembled with the hydride, the tanks are then activated by MAHYTEC.

Figure 7 – Activation of hydride tank (AB5 and AB type).

2.4 Determination of the hydrogen mass inside the hydride tanks

As mentioned, MAHYTEC is not in charge of performing the tank tests. CEA-Liten and FHA are responsible of this task. However, MAHYTEC performed some validation tests of these tanks before the shipment to the project partners. The results are presented in the following.

Firstly, MAHYTEC manufactured an AB5 hydride. The hydrides based on AB5 intermetallic compounds represent the most versatile and commercially important family of reversible hydriding alloys. "A" is usually taken from the rare earth (Lanthanide) elements and "B" is Ni, usually in combination with other transition metals. The AB5s are essentially line compounds (i.e. are rather closely restricted to the atomic A:B ratio of 1:5). They can be prepared in tonnage quantities by conventional metallurgical techniques such as vacuum induction melting. Like most intermetallic compounds, they are very brittle and easily reduced to the granular or powder form required for the filling of hydride containers.

2.4.1 Method 1: Weighing method

To realise the test with AB5, the tank was filled with a pressure of 10 bar. Afterwards the tank was weighed once full of hydrogen. Under constant temperature (T = 22 °C), the pressure and the mass into the tank, before removing 0.1 g of H_2 at regular time intervals, was measured.

Characteristics of device:

Scale: max 750 g, e = 0.01 g, d = 0.001 g

Digital pressure gauge: EM: -1 … 30 bar, error: ± 0.2%

Condition test:

Loading: $P_{loading}$ = 10 bar and $T_{loading}$ = 22 °C

Unloading: $T_{Unloading}$ = 22 °C

Figure 8 – Picture of the weighing scale at MAHYTEC.

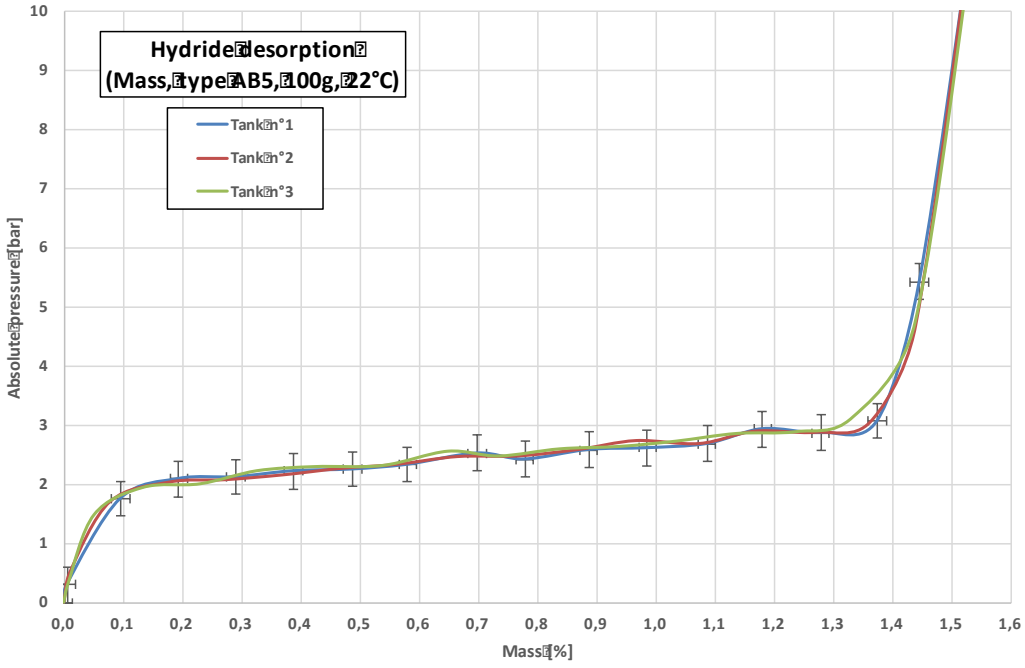

Figure 9 – Curve Pressure vs capacity for the three AB5 tanks.

MAHYTEC has replaced the initial hydride tank (AB5) by an AB type hydride. Most of the practical AB compounds are based on TiFe and therefore represent low raw materials costs. The AB compounds are generally much more difficult to activate than the AB5 compounds, partly a result of more passive and dissociative inactive natural oxide Films on the surface of air-exposed particles and partly the result of higher toughness. In any event, activation of TiFe-type alloys typically takes tens of hours at high pressure vs. tens of minutes at lower pressures for many of the AB5 compounds.

Table 1 – A comparison of the two hydrides (AB5 and AB).

	H capacity	PCT	Activation	Impurity Effects	Cyclic Stability	Ease of manufacture	Pyrophoricity	Cost
AB_5	0	+	+	+	+	+	0	0
AB	0	+	-	-	-	+	+	+

When hydride is activated, it can be loaded with a maximum pressure at 15 bar. The comportment (PCT) of this hydride is very similar of the AB5. The principle difference is the flow kinetic which is lower and a degradation of the hydride on the 20 first cycles. It is very important to use a high-quality hydrogen (quality > 99.995%).

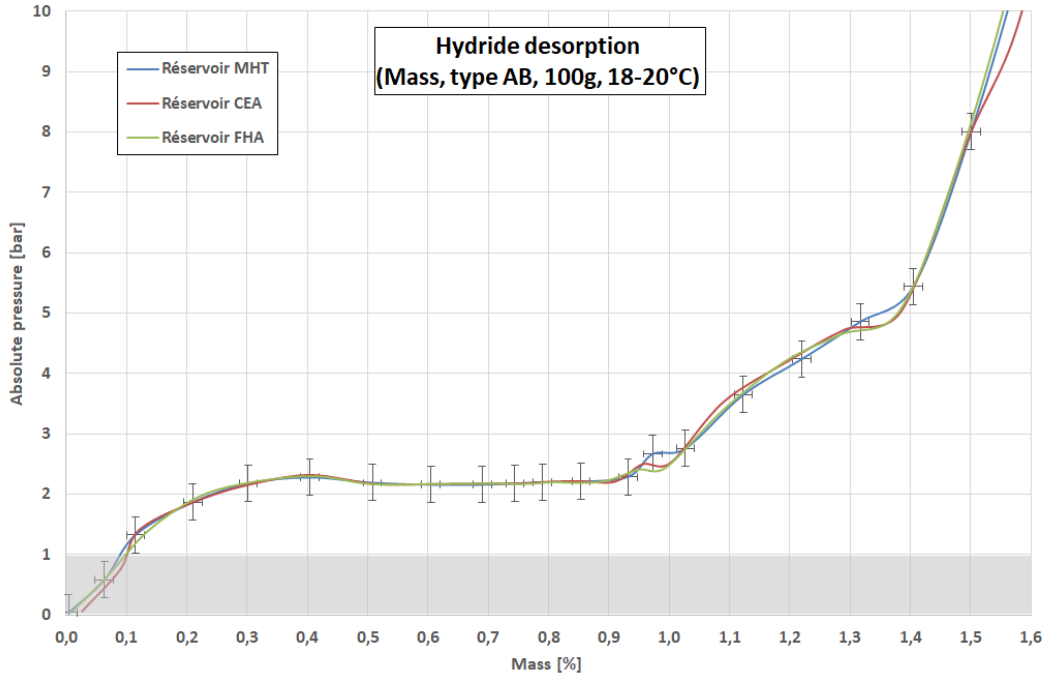

Figure 10 – Curve Pressure vs capacity for the three AB tanks.

The comparison between each of the three tanks gives similar results. In this case we conclude that all the tanks were activated correctly. The tanks were used by the partner (FHA and CEA).

With this method, it was observed that the results are similar. The three tanks behave the same way. This method is reliable but cannot be applied for cycle tests and for large tanks because of the high ratio between the weight of a tank and the mass of hydrogen stored.

2.4.2 Method 2: Flow rate measurement (at the example of AB5)

The first method (weighing method) gives the best result but it's not realizable as an industrial method. The ratio between the tank and the hydrogen in the tank is too large. The second method is the most appropriate but not the most reliable. The mass flowmeter method is the best solution, but it is necessary to respect the usual preconisation.

MAHYTEC realised the flow rate measurement method only for discharge (unload) of the tank. The temperature was measured on the surface of the tank, the output pressure and the flow of hydrogen. At the output of the tank, a pressure regulator set at 0.45 bar was used. The flow meter has always the same pressure at this input. In this case, no controller for the mass flow is needed because the pressure is constant. A needle valve is sufficient to fix the constant flow between 5 NmL/min and 40 NmL/min. A check valve at the output of the system prevents from a return of air into the tank and from polluting the hydride. In this test bench the dead volume of the pipes is very low. This helps to reduce the error due to this volume.

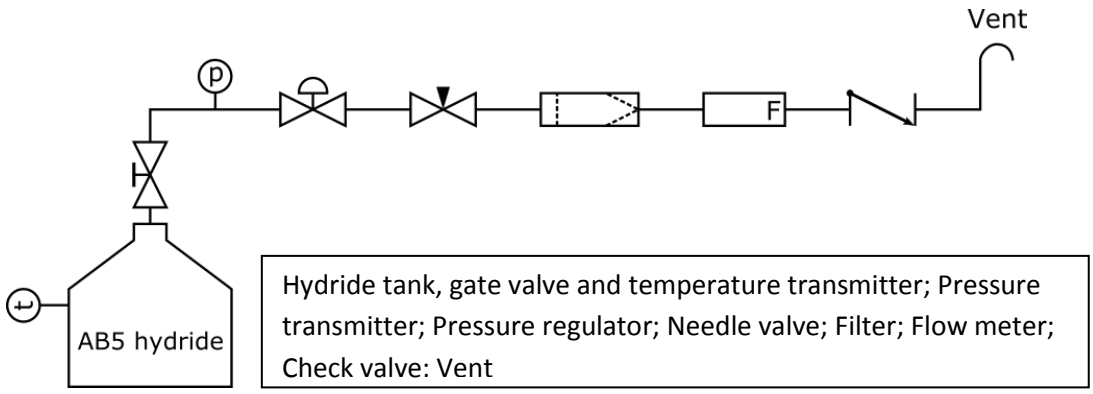

Figure 11 – P&ID of the flow measurement test bench at MAHYTEC.

- Thermocouple T on the tank
- Pressure sensor: 15 bar max
- Output Pressure Regulator: 0 to 1 bar
- Needle valve: Cv = 0.004
- Flowmeter: 65 NmL/min max

Figure 12 – Picture of the flow measurement test bench at MAHYTEC.

It can be seen that the curve below is very similar to the one obtained with the mass method, the abscissa axis being here the volume of desorbed hydrogen. The flow rate is here set at 5 mL/min.

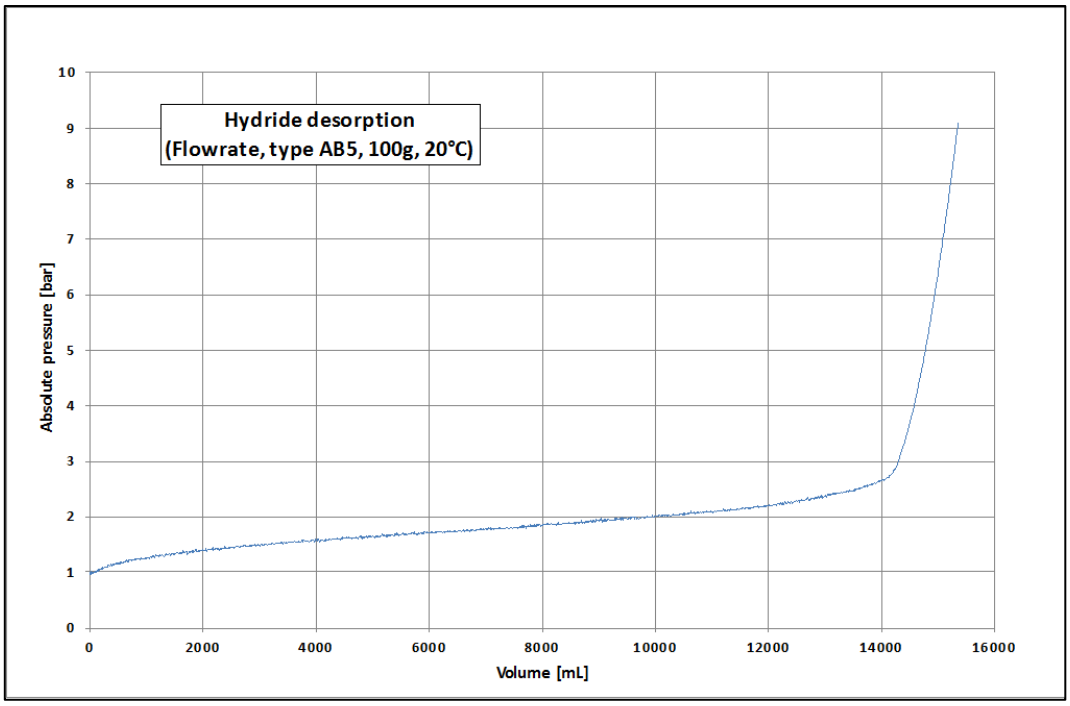

Figure 13 – Measurement result for the discharge of the tank with 5 NmL/min.

In addition, this method makes it possible to visualize on the graph below the evolution of the temperature (red curve), the flow (blue curve) as well as the pressure (green curve) over time. Fluctuations in the flow rate come from a setting of the needle valve during the measurement.

It is found that the desorption phenomenon, despite a very low flow rate, still causes a drop-in temperature which stabilizes at thermal equilibrium before returning to room temperature.

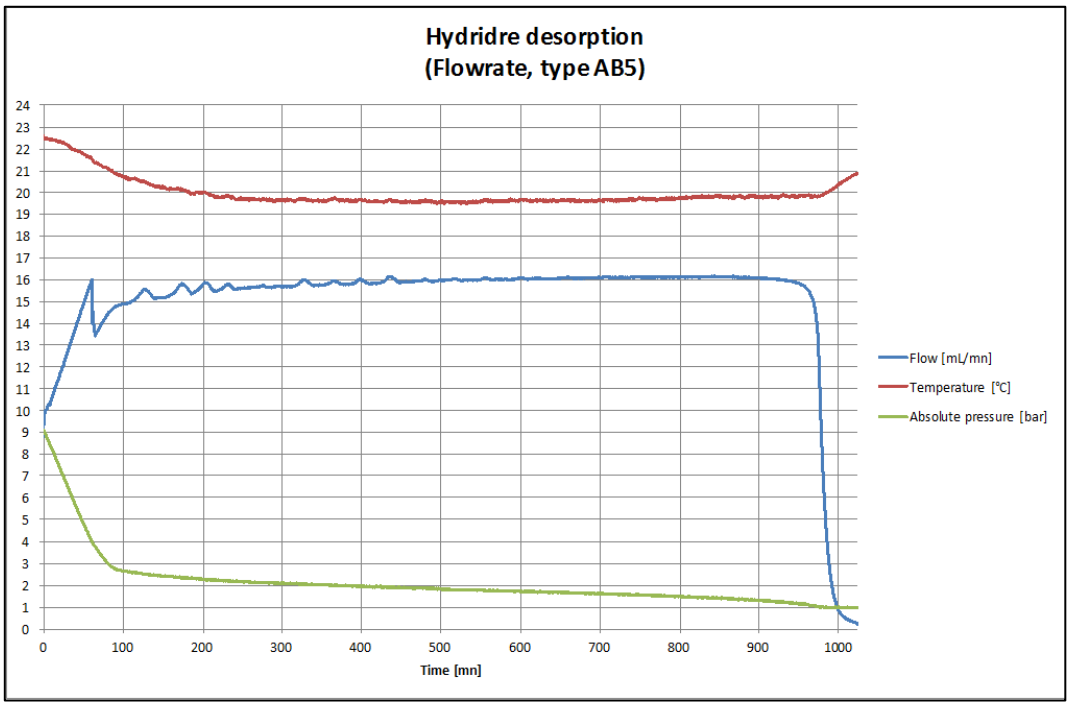

Figure 14 – Flow, pressure and temperature during discharge of the tank (15 NmL/min).

3 FHA (Aragon Hydrogen Foundation)

The Foundation for the Development of New Technologies in Aragon is a private, not-for-profit entity, created to promote the use of hydrogen as an energy vector.

Promoted by the Government of Aragon, it was founded in 2004 with the support of the administration, industry and the main society actors from different sectors of activity.

The mission of the foundation is to carry out the organization, management and execution of a wide range of actions with the purpose of generating, storing and transporting hydrogen for its use in fuel cells, in transport applications or for the generation of distributed energy.

3.1 Measurements with AB5

3.1.1 Measurement set-up

The measurement set-up makes it possible to measure the flow during charge and discharge of the hydrogen tank provided by MAHYTEC.

Piping and Instrumentation Diagram (P&ID):

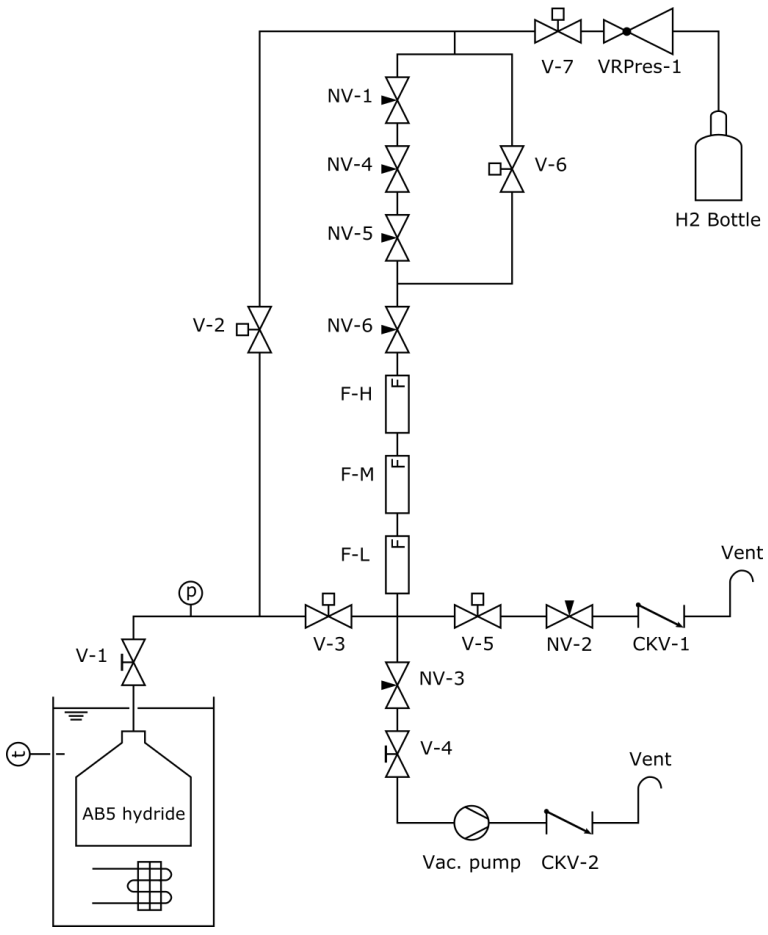

Figure 15 – P&ID diagram of the test rig at FHA.

Rig Employed Components:

1. Tubing: ¼" OD
2. V-1, V-4: Manual valve; HB1H-4T; ¼" OD
3. VRPres-1: Manual regulating pressure valve; Air Liquide; RED DLM 300 200-15-50 TIPO E(NF) DA 6 MM: P_{max} in: 200bar; P_{reg} out: 0 – 15 bar; Nominal flow (N_2): 50 Nm3/h
4. V-2, V-3, V-5, V-6, V-7: Solenoid valve; Burkert; 6013 NC ¼" 24cc; PN 0 – 16 bar
5. NV-2, NV-3, NV-6: Needle Valve; ¼" OD HyLok; SANV24HT
6. NV-1: Needle valve; Swagelok; 1/4" OD; SS-SS4-VH; Cv: 0.004
7. NV-4, NV-5: Needle Valve; 1/8" NPT HyLok; NV1F-2N-R Regulating
8. CKV-1: Check Valve; ¼" OD; HyLok; VITON 1psi; SACV14HT1
9. Flowmeter-H: Bronkhorst; F-111BI-RGD-22-V; 0 – 25 NL/min H_2; 10 bara; 20 °C; Accuracy: ± 0.5% Rd ± 0.1% FS; Temp sensitivity: [± 0.05% Rd ± 0.05% FS] /°C; Pressure sensitivity: ±0.01% Rd /bar
10. Flowmeter-M: OMEGA; FMA1712A-H_2-10barA/9.5barA; 0 – 500 SCCM (0 – 463 NmL/min); Accuracy: ± 1.0% FS; Repeatability: ± 0.25%; Temp sensitivity: [± 0.15% FS] /°C; Pressure sensitivity: ±0.01% FS /0.07 bar
11. Flowmeter-L: OMEGA; FMA1704A-H_2-2barA/1barA; 0 – 20 SCCM (0 – 18.55 NmL/min); Accuracy: ± 1.0% FS; Repeatability: ± 0.25%; Temp sensitivity: [± 0.15% FS] /°C; Pressure sensitivity: ± 0.01% FS /0.07 bar
12. Pressure transmitter: BAUMER; ½" NPT; 0 – 16 bar; CTX369B24A
13. Vacuum pump: DINTER; Mod. D-95; 750 mmHg vac.
14. Metal hydride water bath: LT ecocool 100; Temperature stability: ± 0.05 °C
15. Hydrogen: Linde 5.0 (Purity ≥ 99.999%, Impurities [ppm]: $H_2O \leq 3$; $O_2 \leq 2$; $C_nH_m \leq 0.5$; $N_2 \leq 5$

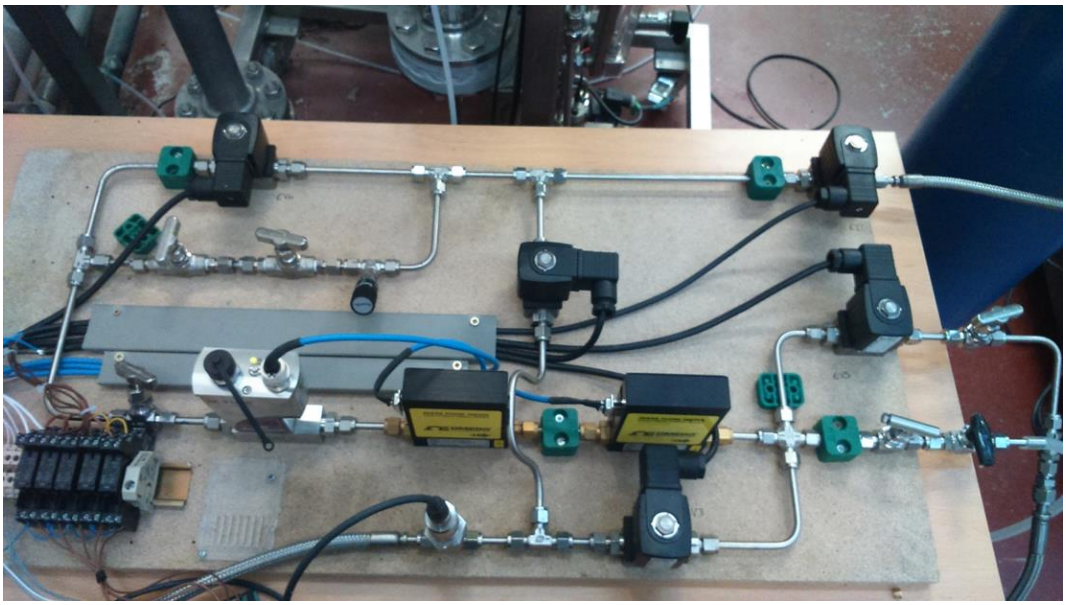

Figure 16 – Picture of the measurement set-up at FHA.

3.1.2 Working principle

This system is designed to measure the flow of hydrogen with three flowmeters during the charge and the discharge. The flow is not controlled; it is only limited by the needle valves to have the flow always inside the range of the three flowmeters. There is installed a manual pressure regulating valve (VRPres-1) which connects the hydrogen bottle, which feeds the tank, to a hose and the system (hose situated on the upside of the photo).

As the difference of pressure between the output of the pressure regulator and the hydrogen tank is in the beginning, high and, in the end slow, the flow had a peak in the beginning and went down with the time. The same occurs in the discharge between the system and the vent. With the new 3 added valves (NV-4, NV-5 and NV-6), the first peak in the charge has been deleted although when V-6 is opened another peak appears not only in charge but also in discharge.

As we observed that the peak of the discharge beginning was too high, we added another needle valve just before the vent (NV-2).

In order to reduce as much as possible, the first peaks of the charge and the discharge, the needle valve NV-1 is totally closed, NV-2, NV-4, NV-5 and NV-6 are close to be totally closed. Special care has to be taken in the case of NV-6 and NV-2 because if they are too closed, too much residual pressure can be retained thus lot of hydrogen stay into the metal hydride tank.

The way the flow measurement work is taking always the measurement of the higher flow from the three flowmeters.

The hydride tank is connected by a hose to the system (bottom of the photo) and submerged in a recirculated water bath with the temperature controlled by a cryostat with an accuracy of 0.1 °C.

3.1.3 Cycle testing

The needle valve NV-2 is regulated to have a slow peak of flow during the discharge.

The needle valve NV-3 and the shut-off valve V-4 are used open only when vacuum is necessary so during the charge/discharge cycles are totally closed. (You can see them at the right of the photograph).

V-1 is the shut-off valve incorporated in the hydride tank hence, during the tests is open.

Charge

1. Pressure Reducing Valve (VRPres-1) with an output pressure 0.1 – 0.2 bar above the set point pressure (12 barg)
2. All valves closed
3. Open V-1, V-3, V-7 → charge begins
4. When set pressure*) reached (5 barg)→ V-6 open (Needle valves restriction bypassed)
5. Charge finished when flow < 1NmL/min
6. All valves closed

*) Pressure at which the V-6 is opened has been chosen because it is in the middle between the set point pressure of F-L (1 barg) and the two other flow meters F-M and F-H (9 barg) so that the error, caused by the difference of pressure, is reduced.

In the beginning, due to the low flow conditions, only the measurement values of F-L are taken into consideration. When V-6 will be opened, the flowrate increases and from then on the reading are taken from F-M and F-H, respectively.

Discharge

1. Open V-2 and V-5
2. Open V-6 when pressure < X barg **)
3. Discharge finished when flow < 1 NmL/min and pressure < X barg
4. All valves closed

**) The pressure value X will be selected for the best discharge situation.

Some side notes:

1. When we only used the pressure as indicator whether the tank is filled, the volume of hydrogen charged is for the most cases too low.
2. The flowmeter of 500 SmL/min and 20 SmL/min are adjusted because the *standard conditions* for them are: 21.1 °C and 1.01 bar whereas for the flowmeter of 25 NL/min the *normal conditions* are: 0 °C and 1.013 bar. It can thus be concluded that the maximum flows measured by F-M and F-L are 463.5 NmL/min and 18.54 NmL/min, respectively.

3.1.4 Measurement results (AB5)

Test n°0:

Test n°0 is constituted of 10 cycles. Before test n°0 was performed the system has been adjusted while the hydride metal tank was closed in order to achieve that all measurements could be performed only with two flowmeters (F-L and F-M from OMEGA). However, it was not possible to eliminate the well-known first flow peak when the tank was unloaded.

For the three first cycles, minor adjustments for the needle valves regarding the set point pressures were necessary. Attempts were made to open V-6 at an optimal system pressure value, so that the first flow peak (directly after start of charging) can be reduced to a minimum. On the other hand, it should remain possible to reach the 12 barg at the end of the load process and 0 barg at the end of the unload process, respectively. NV-6 cannot be as closed as to cause a difference of pressure between the inlet and the metal hydride tank enough to not achieve the 12 barg in the load. A similar consideration has to be taken in account with the sum of this effect in the NV-6 and NV-2 to achieve a final pressure close to zero in the unloading.

The other seven of the ten cycles had the following characteristics:

- Temperature: 22 °C
- Load V-6 opening: 11.67 barg
- Unload V-6 opening: 1.3 barg
- Flow to finish load: 1 NmL/min
- Flow to finish unload: 0.5 NmL/min
- Load measured volume: 11329.54 NmL
- Unload measured volume: 12971.93 NmL

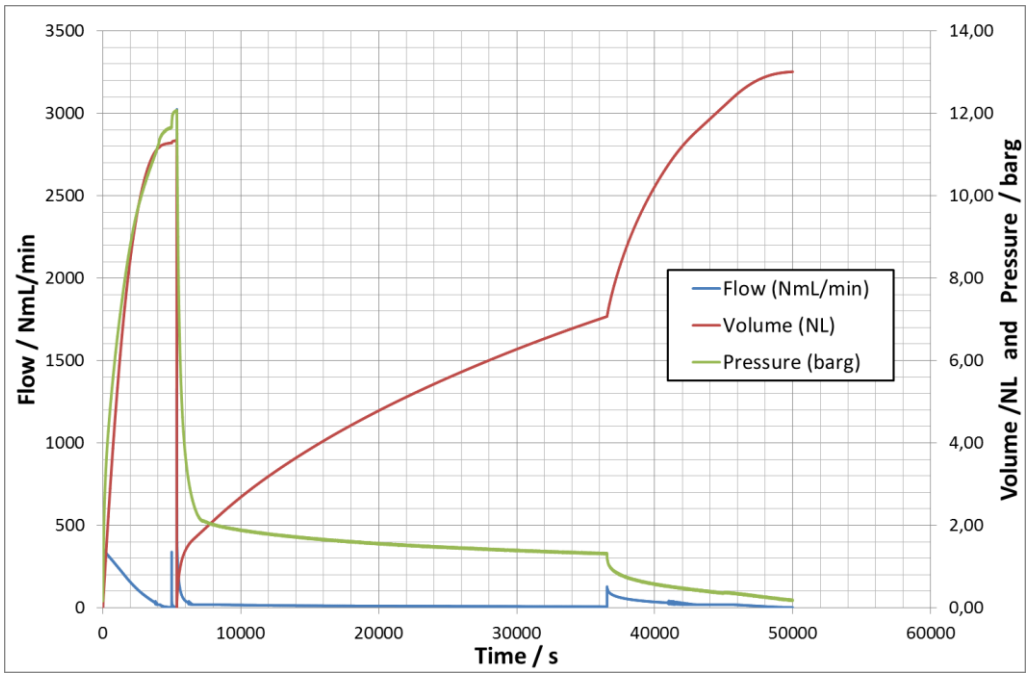

Figure 17 – Measurement result of initial test n°0.

Update after test n°0:

The next tests are focused in measure the flow with the flowmeter whose set point pressure is the closest with respect to the pressure at which this flow is being measured. For instance, until the pressure does not reach 5 barg the flow is measured with F-L as its set point pressure is 1 barg and the F-M and F-H have a set point pressure of 9 barg.

Test n°1:

The test was performed under the following conditions:

- Temperature: 22 °C
- Load V-6 opening: 5 barg
- Unload V-6 opening: 8 barg
- Flow to finish load: 1 NmL/min
- Flow to finish unload: 0.5 NmL/min
- Load measured volume: 15214.93 NmL
- Unload measured volume: 11917.33

After the analysis of the data a failure during the load cycles was detected: F-L was measuring for a long period of time above its nominal flow rate. (This conversely means that the totalized volume is obviously too low for the load (charge) cycle.).

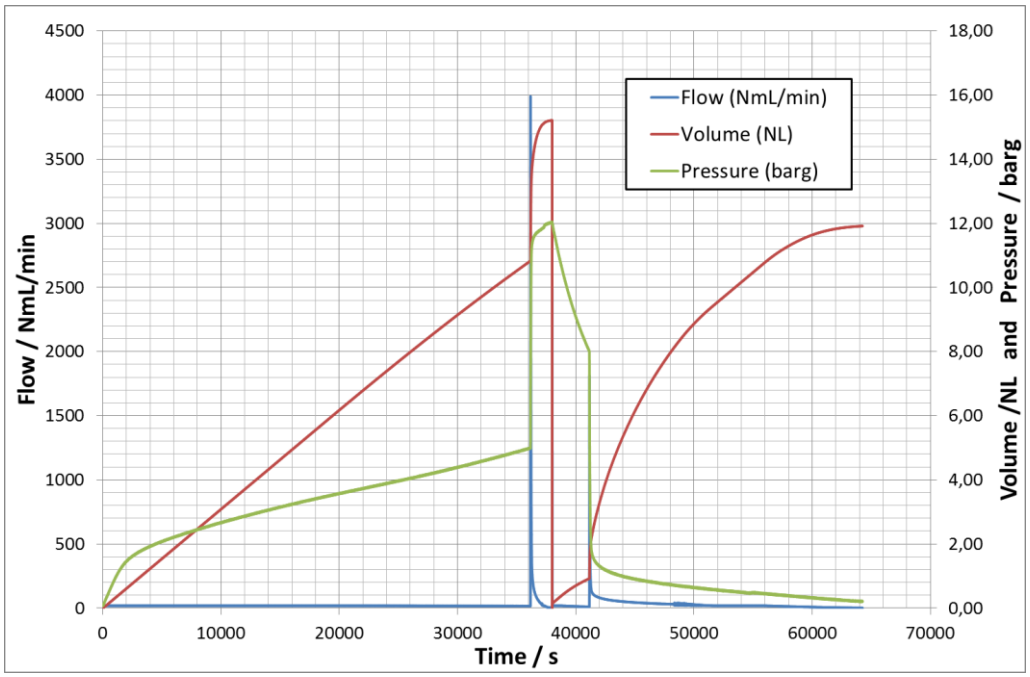

Figure 18 – Measurement result of test n°1.

Update after test n°1:

1. To overcome the above-mentioned problem the needle valves NV-4 and NV-5 were slightly closed a bit more to reduce the initial flow, so that F-L measures within its specification.

2. NV-2 was also closed a bit more to reduce the flow during the unload process (discharge).

Test n°2:

The test was performed under the following conditions:

- Temperature: 22 °C
- Load V-6 opening: 5 barg
- Unload V-6 opening: 5.5 barg
- Flow to finish load: 1 NmL/min
- Flow to finish unload: 1 NmL/min
- Load measured volume: 15488.0 NmL
- Unload measured volume: 13491.0 NmL

Note: Only the first cycle of test n°2 was analysed.

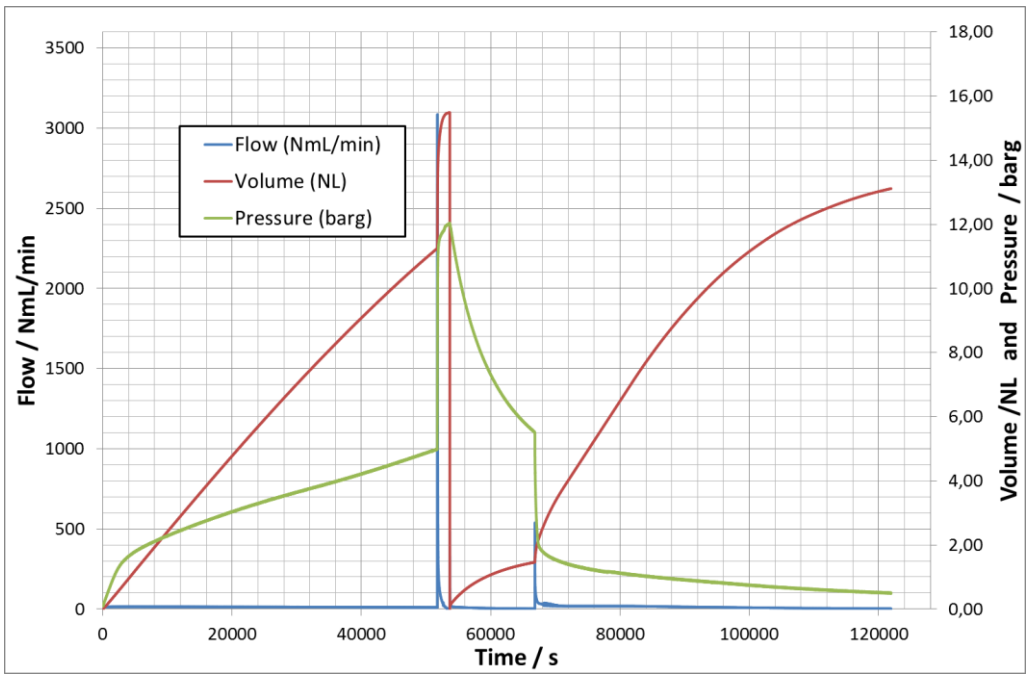

Figure 19 – Measurement result of test n°2.

Update after test n°2:
Make the unload process faster by changing the opening pressure of V-6 to 10 bar.

Test n°3:

The test was performed under the following conditions:

- Temperature: 22 °C
- Load V-6 opening: 5 barg
- Unload V-6 opening: 10 barg
- Flow to finish load: 1 NmL/min
- Flow to finish unload: 1 NmL/min
- Load measured volume: 14947.6 NmL
- Unload measured volume: 13230.16 NmL

Note: The first 6 cycles of test n°3 were analysed.

The difference of measured volumes (between test n°2 and test n°3) is that the initial pressure in test n°2 was 0.1 bar and in test n°3, 0.4 bar. The reason is that NV-2 does not allow discharging the entire pressure in the hydride tank.

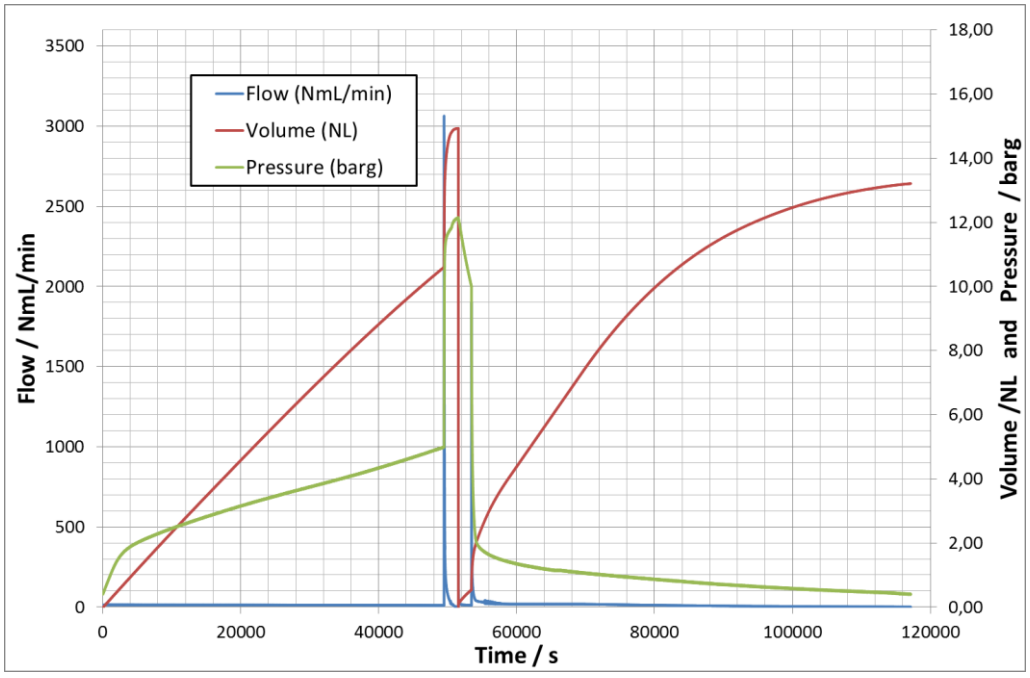

Figure 20 – Measurement result of test n°3.

Test n°4:

The test was performed under the following conditions:

- Temperature: 22 °C
- Load V-6 opening: 5 barg
- Unload V-6 opening: 11.9 barg
- Flow to finish load: 1 NmL/min
- Flow to finish unload: 1 NmL/min
- Load measured volume: 15329.5 NmL
- Unload measured volume: 12312.17 NmL

Note: The first 3 cycles of test n°4 were analysed.

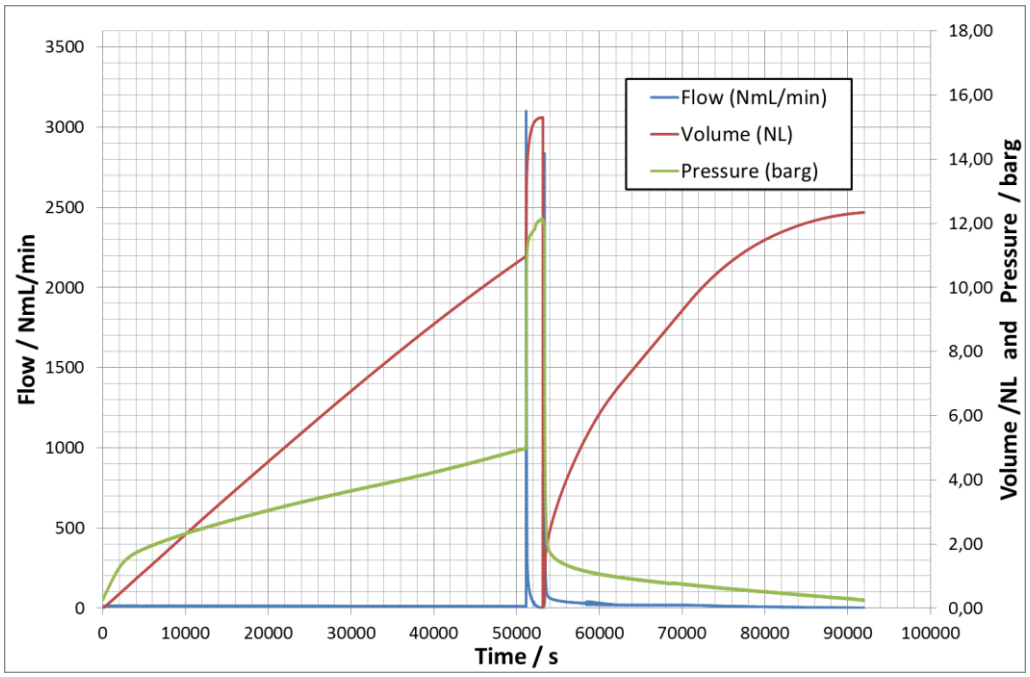

Figure 21 – Measurement result of test n°4.

Test n°5:

The test was performed under the following conditions:

- Temperature: 35 °C
- Load V-6 opening: 5 barg
- Unload V-6 opening: 11.9 barg
- Flow to finish load: 1 NmL/min
- Flow to finish unload: 1 NmL/min
- Load measured volume: 13450.6 NmL
- Unload measured volume: 11370.8 NmL

Note: The first 4 cycles of test n°5 were analysed.

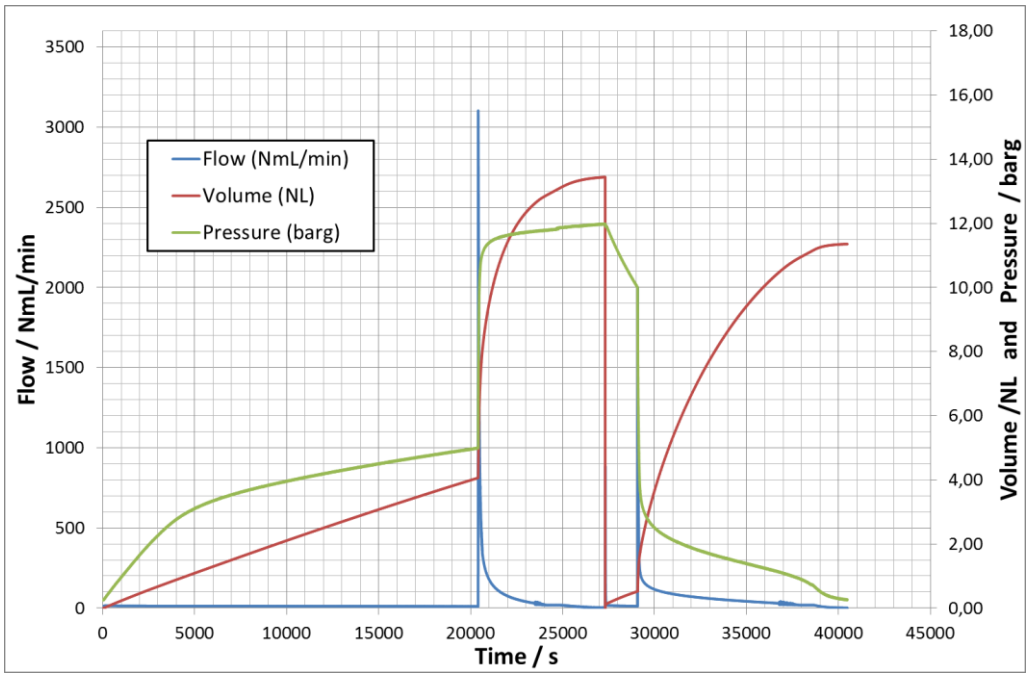

Figure 22 – Measurement result of test n°5.

Update after test n°5:

As it is observed, when the chosen pressure is higher, the measured volume in the discharge is lower. In order to improve the results, similar test to test n°2 were performed with the difference of that the needle valve NV-2 is more opened to try to eliminate the residual pressure in the tank (0.4 barg) and the pressure at which the valve V-6 is opened is 5.2 instead of 5.5 barg.

Test n°6:

The test was performed under the following conditions:

- Temperature: 22 °C
- Load V-6 opening: 5 barg
- Unload V-6 opening: 5.2 barg
- Flow to finish load: 1 NmL/min
- Flow to finish unload: 1 NmL/min
- Load measured volume: 15287.7 NmL
- Unload measured volume: 12123.8 NmL

Note: Test n°6 had 5 cycles but only 4 cycles have been analysed. The first cycle does not have modified the NV-2 so this cycle is not included in this analysis.

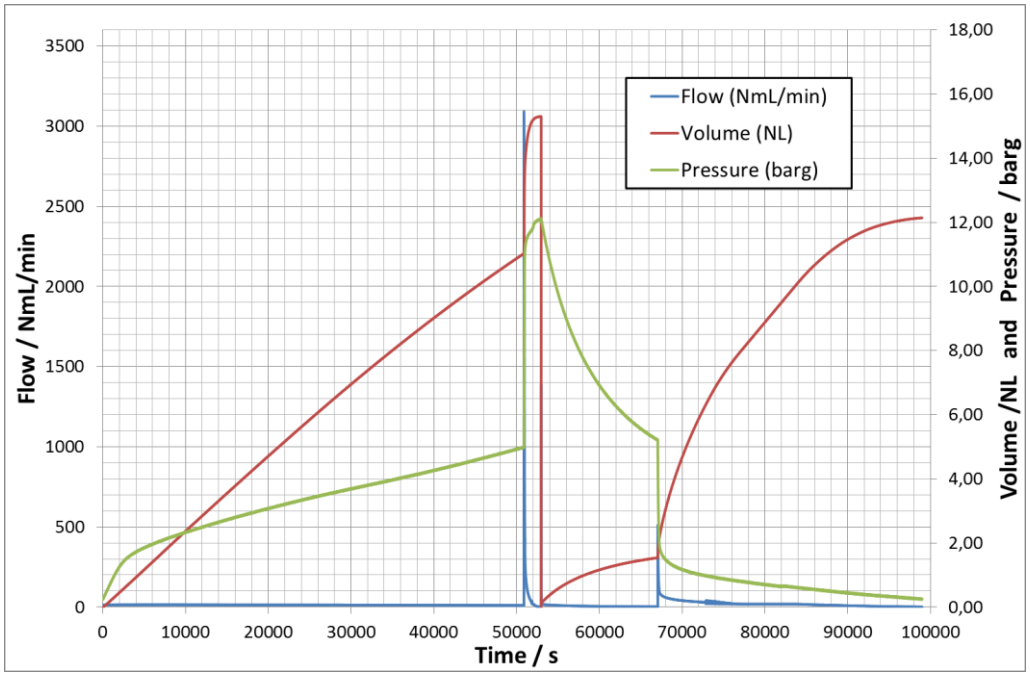

Figure 23 – Measurement result of test n°6.

Summary of the results:

Table 2 – Summary of the measurement results from test n°0 to test n°6

	Test n°0	Test n°1	Test n°2	Test n°3	Test n°4	Test n°5	Test n°6
Temp. °C	22	22	22	22	22	35	22
Volume (load) NmL	11329.5	15214.9	15488.0	14947.6	15329.5	13450.6	15287.7
Volume (unload) NmL	12971.93	11917.33	13491.0	13230.2	12312.2	11370.8	12123.8
Deviation %	-14.5	+21.7	+12.9	+11.5	+19.7	+15.5	+20.7

As it can be seen from Table 2 – Summary of the measurement results from test n°0 to test n°6, the measured volume during charge (load) is in all cases (except for test n°0) less than the measured volume during discharge (unload).

3.1.5 Discussion after the tests with AB5

Indicated main issues:

A. Big changes of flow cause loss of volume measured:
In the hydride tank during unloading, the flowmeter F-M has not a good measurement in the range of 19 – 30 NmL/min (many fluctuations) and the flowmeter F-L is measuring in a saturated state. These measurements are performed during a large period of time and there is consequently a lot of discharged hydrogen volume that is not measured.

→ *This is probably the major cause if we also look at the volume measured in test n°0.*

B. Dead volume effect

Fluctuation in the flow rate reading

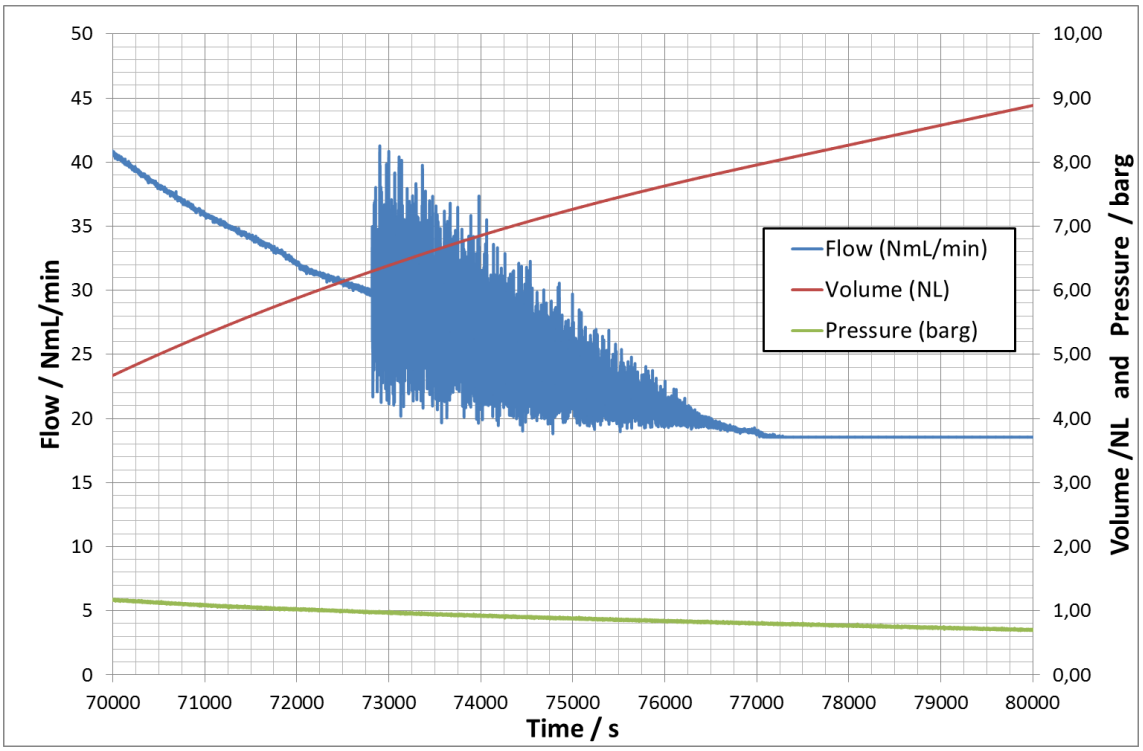

Figure 24 – Enlarged view of test n°6 (see Figure 23).

As it can be seen in **Figure 24** the flowmeter F-M shows large fluctuations at flow rates between 19 and 30 NmL/min. At the end it is most probably not a real problem as the mean value is apparently close to the actual flow rate.

Dead volume effect

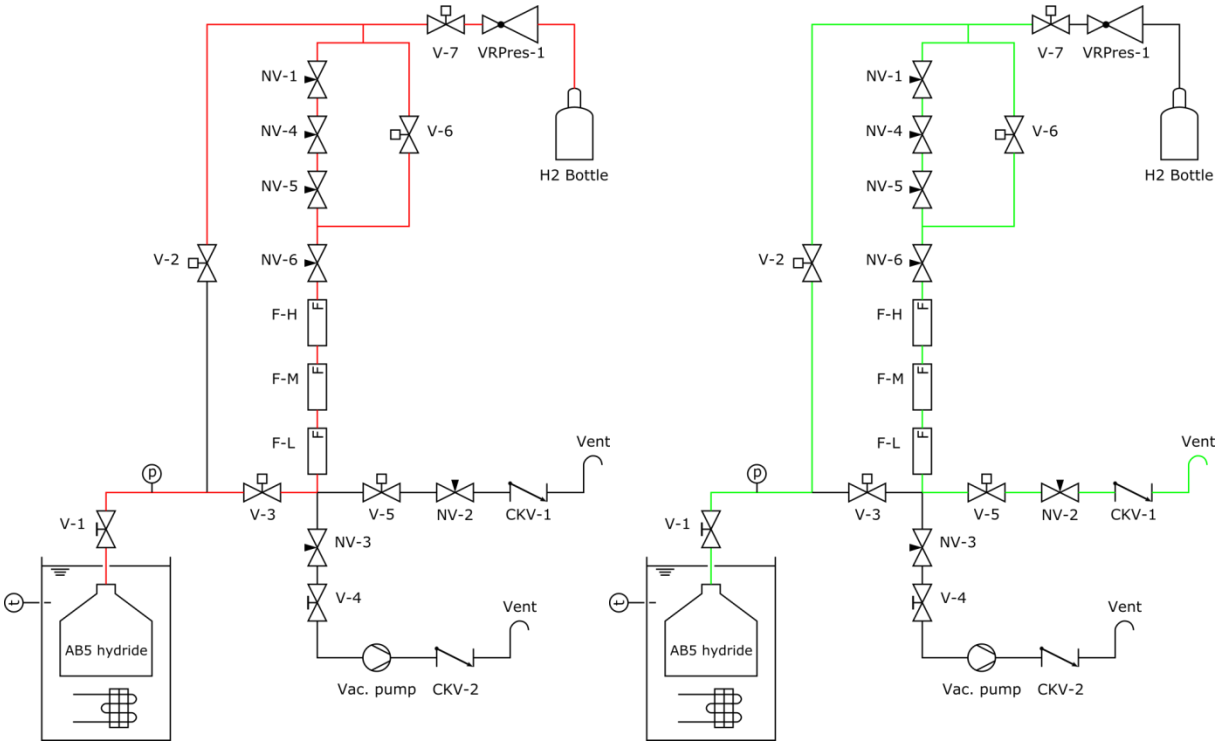

Figure 25 – left: load (charge); right: unload (discharge).

Charge

As it can be seen in **Figure 25** (left drawing) at the end of the charge process, there is hydrogen which has passed the flow meters but has not entered the tank. At the end of the charge process the flow reading comes mainly from F-H (largest distance to the tank) and the pressure is quite high.
►That means an *overestimation* of the mass (volume) in the tank.

Discharge

As it can be seen in **Figure 25** (right drawing) at the end of the discharge process, there is hydrogen which has left the tank but will not passes the flow meters. At the end of the discharge process the flow reading comes mainly from F-L (largest distance to the tank) and the distance to the flow meter (inclusive the by-pass with V-6) is already quite large.
►That means an *underestimation* of the mass (volume) in the tank.

Both effects are obviously counter-productive. That means in the first case (charge) the determined mass (volume) in the tank is too large and in the second case (discharge) the determined mass from the tank is too low. That results in a large “error” for the charge/discharge ratio.

3.2 Measurements with AB

3.2.1 Measurement set-up

From the experiences with the measurements of the AB tank the test rig was modified. It was decided to install an additional needle valve after the flowmeters in order to maintain the pressure as constant as possible, that means to avoid the Δp effect. The first flow peak appears in the beginning of the charge period due to the removal of the needle valves between the hydrogen inlet and the flowmeters. Nonetheless, this peak is very short and will be considered as part of the dead volume. In the case of the discharge line, a pressure regulator and a needle valve were added. They only affect the hydrogen flow in the discharge period and help to maintain a quite constant flow and pressure in the flowmeters zone. The flow peak which exists in the beginning of the discharge period is caused by the hydrogen retained between the outlet and the valves V-2 and V-3 and is also considered to determine the dead volume.

Piping and Instrumentation Diagram (P&ID):

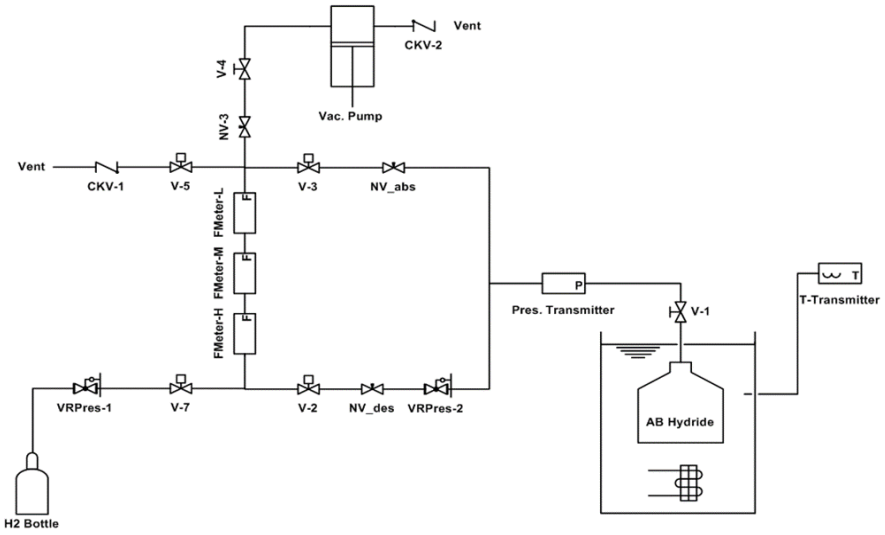

Figure 26 – P&ID diagram of the test rig at FHA.

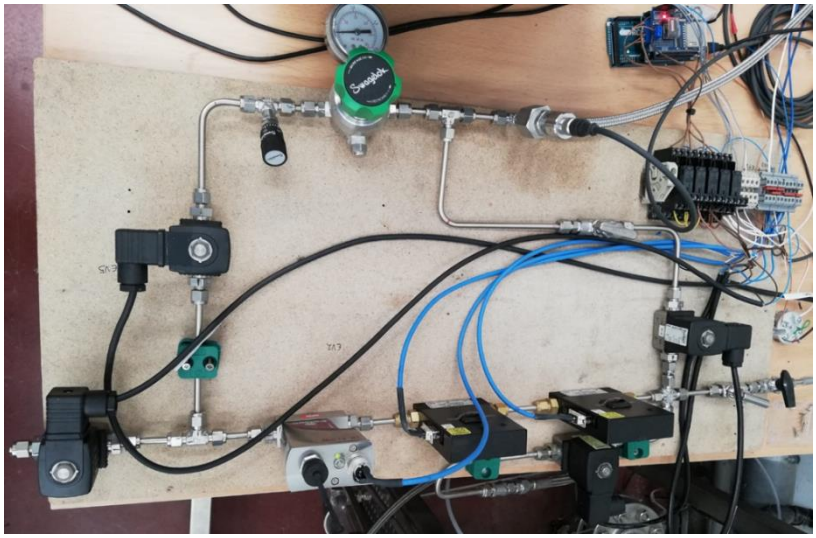

Figure 27 – Picture of the improved measurement set-up at FHA.

Rig Employed Components:

1. Tubing: ¼" OD
2. V-1, V-4: Manual valve; HB1H-4T; ¼" OD
3. VRPres-1: Manual regulating pressure valve; Air Liquide; RED DLM 300 200-15-50 TIPO E(NF) DA 6 MM: P_{max} in: 200bar; P_{reg} out: 0 – 15 bar; Nominal flow (N2): 50 Nm3/h
4. VRPRes-2: Swagelok pressure reducer
5. V-2, V-3, V-5, V-6, V-7: Solenoid valve; Burkert; 6013 NC ¼" 24cc; PN 0 – 16 bar
6. NV-2, NV-3, NV-6: Needle Valve; ¼" OD HyLok; SANV24HT
7. NV-1: Needle valve; Swagelok; 1/4" OD; SS-SS4-VH; Cv: 0.004
8. NV-4, NV-5: Needle Valve; 1/8" NPT HyLok; NV1F-2N-R Regulating
9. CKV-1: Check Valve; ¼" OD; HyLok; VITON 1psi; SACV14HT1
10. Flowmeter-H: Bronkhorst; F-111BI-RGD-22-V; 0 – 25 NL/min H_2; 10 bara; 20 °C; Accuracy: ± 0.5% Rd ± 0.1% FS; Temp sensitivity: [± 0.05% Rd ± 0.05% FS] /°C; Pressure sensitivity: ±0.01% Rd /bar
11. Flowmeter-M: OMEGA; FMA1712A-H_2-10barA/9.5barA; 0 – 500 SCCM (0 – 463 NmL/min); Accuracy: ± 1.0% FS; Repeatability: ± 0.25%; Temp sensitivity: [± 0.15% FS] /°C; Pressure sensitivity: ±0.01% FS /0.07 bar
12. Flowmeter-L: OMEGA; FMA1704A-H_2-2barA/1barA; 0 – 20 SCCM (0 – 18.55 NmL/min); Accuracy: ± 1.0% FS; Repeatability: ± 0.25%; Temp sensitivity: [± 0.15% FS] /°C; Pressure sensitivity: ± 0.01% FS /0.07 bar
13. Pressure transmitter: BAUMER; ½" NPT; 0 – 16 bar; CTX369B24A
14. Vacuum pump: DINTER; Mod. D-95; 750 mmHg vac.
15. Metal hydride water bath: LT ecocool 100; Temperature stability: ± 0.05 °C
16. Hydrogen: Air Liquide Alphagaz 2 (Purity ≥ 99.9999%, Impurities [ppm-v]: $H_2O \leq 0,5$; $O2 \leq 0,1$; $C_nH_m \leq 0,1$; $CO \leq 0,1$; $CO2 \leq 0,1$

3.2.2 Working principle

The flow is also here not controlled but only limited by the needle valves and the pressure reducer to have the flow always inside the range of the three flowmeters but especially in the range of the flowmeter FMeter-L which has the lowest flow rate range (0 to 18.45 NmL/min). That means FMeter-L measures most of the volume in both cases, the load and the unload stages of each cycle.

As the difference of pressure between the output of the pressure regulator (VRPress-1) and the hydrogen tank at the beginning, high and in the end low, the flow has a peak in the beginning and decreased with time. The same behaviour occurs in the discharge state between the system and the vent. However, in this system these flow peaks are caused by the volume in the pipe lines, as the pressure in the tank barely changes due to the high restrictions implied by the NV_abs, NV_ des needle valves and the VRPres_2 pressure reducer. Only when the discharge or the charge period begins, the occurring short flow peaks are measured by FMeter-H and FMeter-M. Thus, most of the volume is measured by the flow meter FMeter-L with small range.

3.2.3 Cycle testing

The needle valve NV_ abs is regulated to have a flow less than 18 NmL/min. Its main issues are the long time that requires the charge and high-pressure difference between the hydrogen inlet and the final tank pressure. However, this high restriction is also useful to maintain the pressure constant in the flowmeters (the inlet pressure).

The VRPres_2 is regulated to have about 0.5 barg (1.5 bara) at the outlet which makes easier the control of the flow for the NV_des to maintain it below 18 NmL/min and helps to have the flowmeters at the same pressure most of the discharge period.

Charge

1. Pressure Reducing Valve (VRPres-1) with an output pressure of 14-15 barg
   → INLET PRESSSURE
2. All valves closed
3. V-1 is always open
4. Open V-3, V-7 → charge begins
5. When set-point pressure < pressure in the tank and the flow is less than the setpoint flow
   → charge finished.
6. All valves closed

Discharge

1. Open V-2 and V-5
2. When set-point pressure>pressure in the tank and the flow is less than the setpoint flow
   → discharge finished
3. All valves closed

3.2.4 Measurement results (AB)

After a large number of tests, a final configuration has been chosen. The final configuration was optimized regrading pressures and flow rates.

The test was performed under the following conditions:

- Temperature: 22 °C
- Inlet Pressure: 14.5 barg (15.5 bara)
- Flow to finish load: 2 NmL/min
- Pressure defined to finish the load ≥ 11 barg (12 bara)
- Flow to finish unload: 2 NmL/min
- Pressure defined to finish the unload ≤ 0.1 barg (1.1 bara)
- Number of cycles: 13

Result:

- Average Load Volume: 9233.47 NmL
- Average Unload Volume: 9239.14 NmL

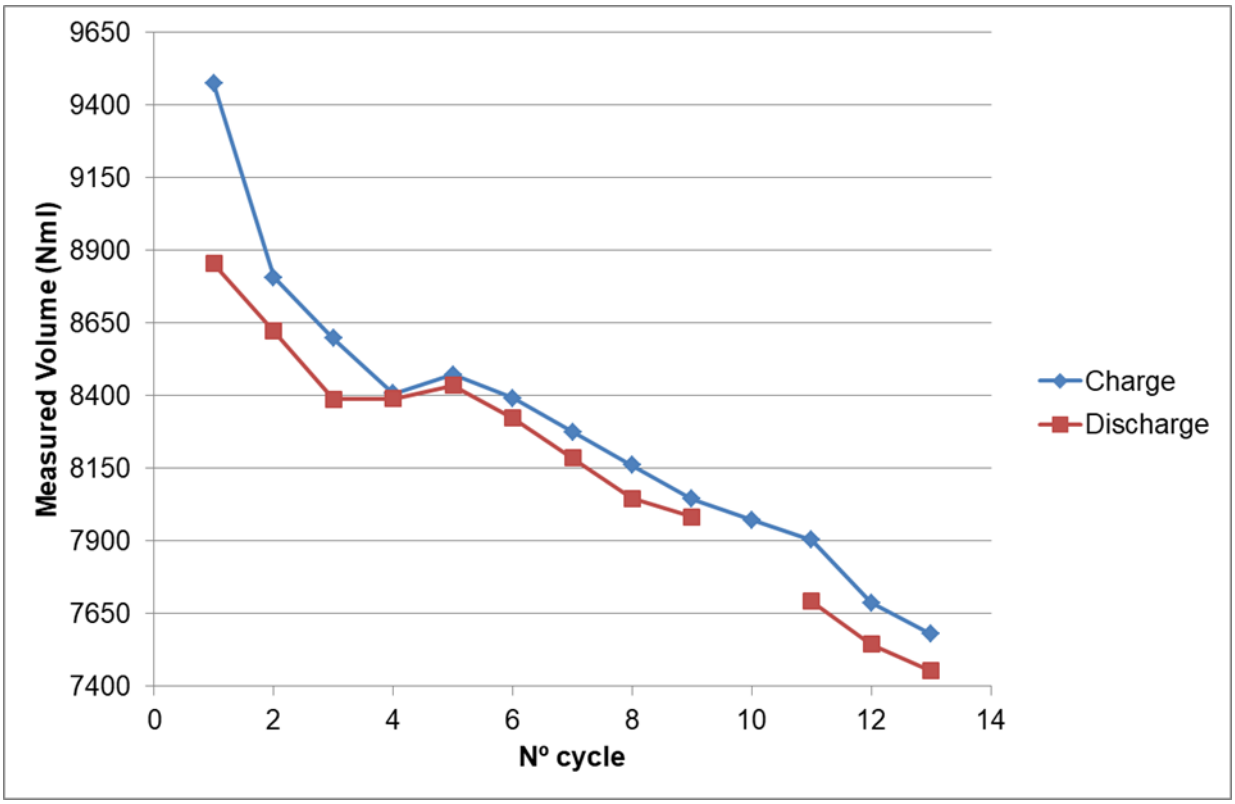

Figure 28 – Measured volume during load and unload for the in total 13 cycles.

Cycle no. 1

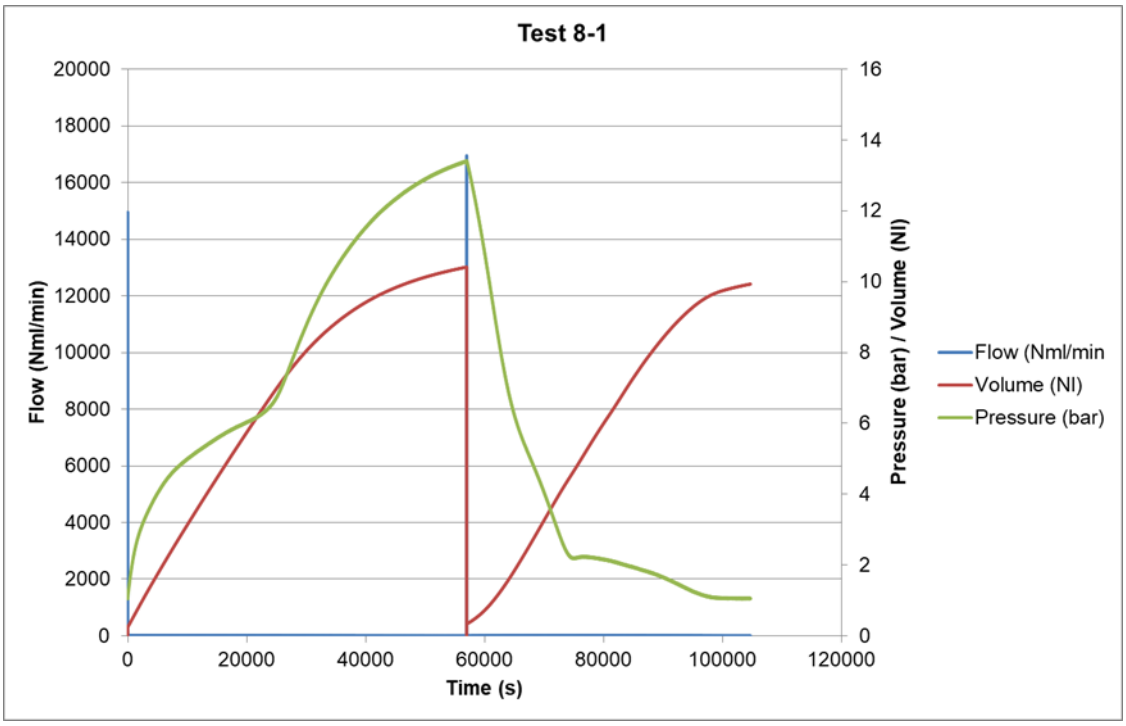

Figure 29 – 1st cycle of the measurement with AB (complete flow rate range).

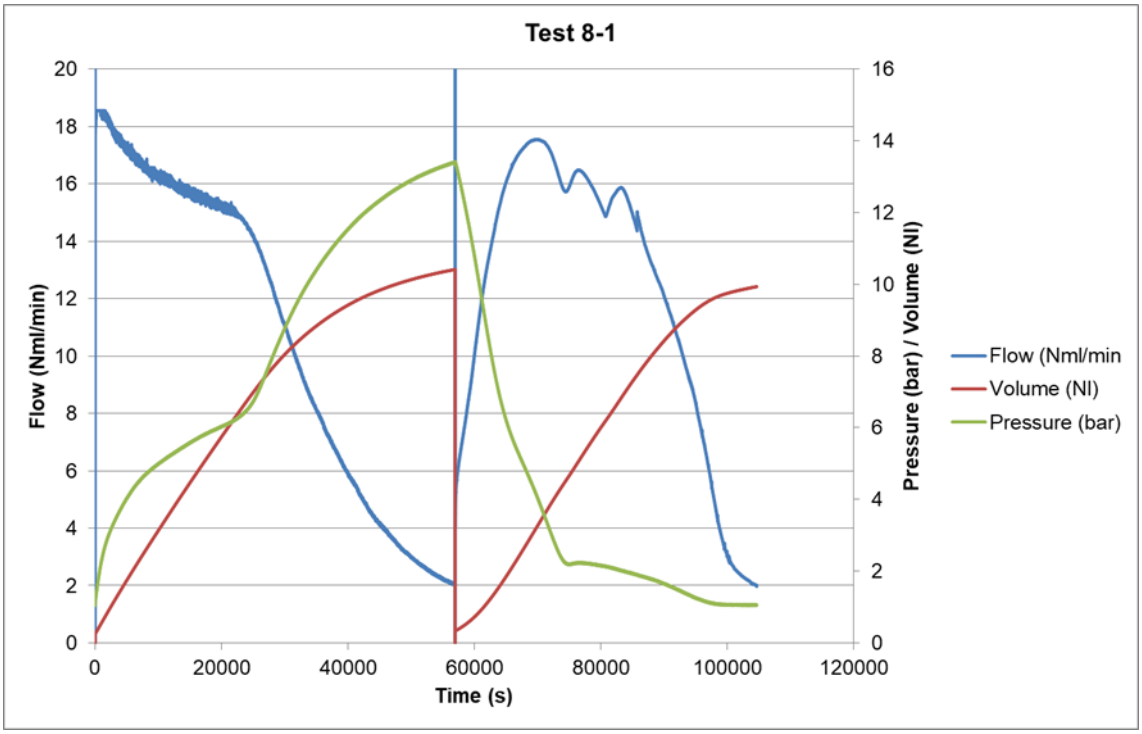

Figure 30 – 1st cycle of the measurement with AB (limited flow rate range).

Cycle no. 13

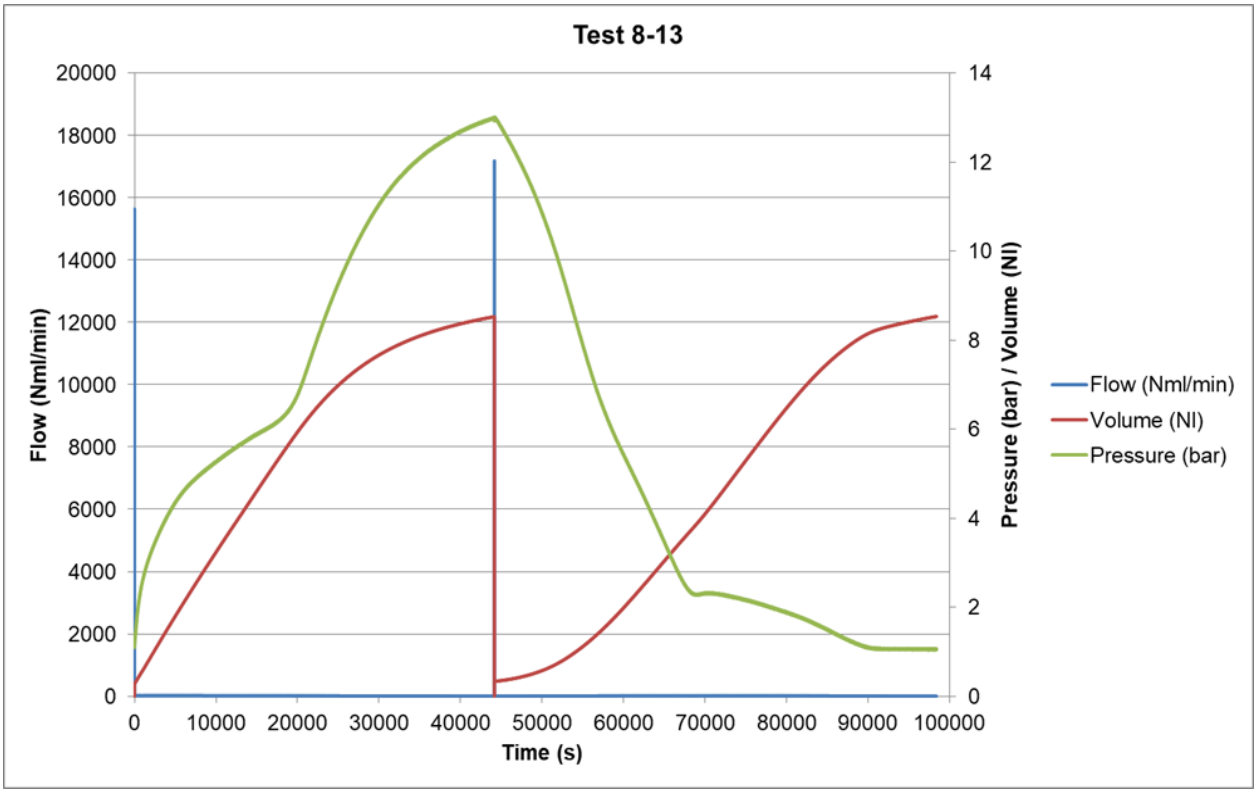

Figure 31 – 13th cycle of the measurement with AB (complete flow rate range).

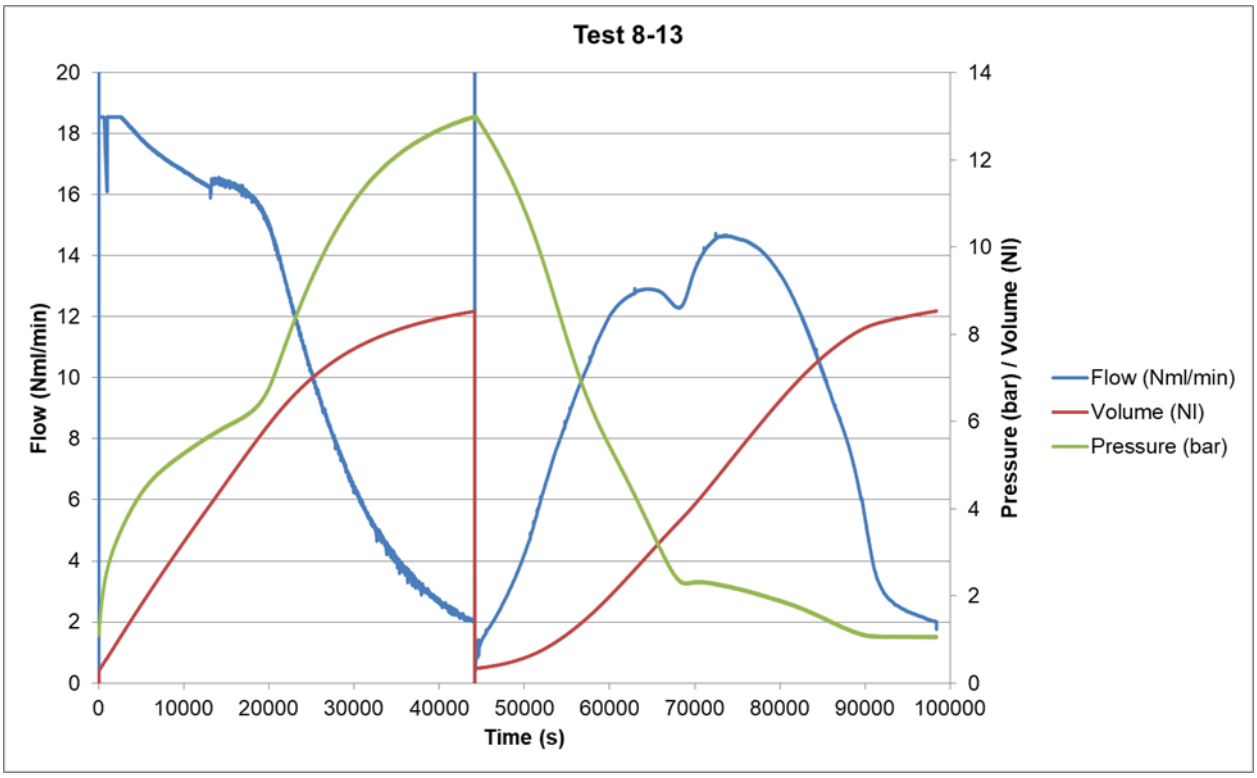

Figure 32 – 13th cycle of the measurement with AB (limited flow rate range).

The results for the in total 13 cycles can be summarized as follow:

Table 3 – Summary of the measurement results from the in total 13 cycles.

Cycle	Average Deviation Load/Unload	Average Deviation Load/Unload (%)
1	438,1934634	4,781947913
2	130,2304049	1,494550149
3	147,3009908	1,734538385
4	13,09968055	0,155986046
5	25,55503911	0,30229119
6	48,64181177	0,58202821
7	62,77903017	0,762794551
8	80,15249741	0,989060801
9	43,53546065	0,543232887
10	0	0
11	149,7146213	1,919962811
12	100,4458412	1,318778482
13	88,93971975	1,183204384
Average:		0,998766172

Determination of the dead volume

This test is aimed at checking any difference of the final flow change in the load from 3 to 2 NmL/min and to see the effect on the volume after performing a large quantity of cycles without stopping the process (letting the tank to desorb hydrogen).

The test was performed under the following conditions:

- Temperature: 22 °C
- Inlet Pressure: 14.5 barg (15.5 bara)
- Flow to finish load: 2 NmL/min
- Pressure defined to finish the load ≥ 11 barg (12 bara)
- Flow to finish unload: 2 NmL/min
- Pressure defined to finish the unload ≤ 0.1 barg (1.1 bara)
- Number of cycles: 10

Result:

- Dead volume load: 943,45 NmL
- Dead volume unload: 1079,27 NmL

These values were applied to the measured volumes in the tests with the AB hydride.

3.2.5 Discussion after the tests with AB

Indicated main issues:

The measured volumes for each cycle (load and unload) are very close.

As it can be seen from **Table 3**, there is a decrease of volume measured with the number of tests/cycles. The reason could be a change in the properties of the AB metal hydride.

The rig set-up was not opened between the different tests. That means it can be excluded that air went into the tank.

Another reason could be the bad performance of the pressure reducer (VRres-1). During the tests a decrease of around 0.4 bar in the hydrogen inlet from cycle n°1 to the cycle n°13 was noted.

Figure 33 – The tank (AB hydride) after the measurement campaign at FHA.

4 CEA-Liten

(French Alternative Energies and Atomic Energy Commission, CEA)

CEA-Liten is a major European research institute and a driving force behind the development of the sustainable energy technologies of future. The institute is spearheading the EU's efforts to limit dependency on fossil fuels and reduce greenhouse gas emissions in three key areas: renewable energy, energy efficiency/storage and development of materials.

4.1 Measurements with AB5

4.1.1 Measurement set-up

Piping and Instrumentation Diagram (P&ID):

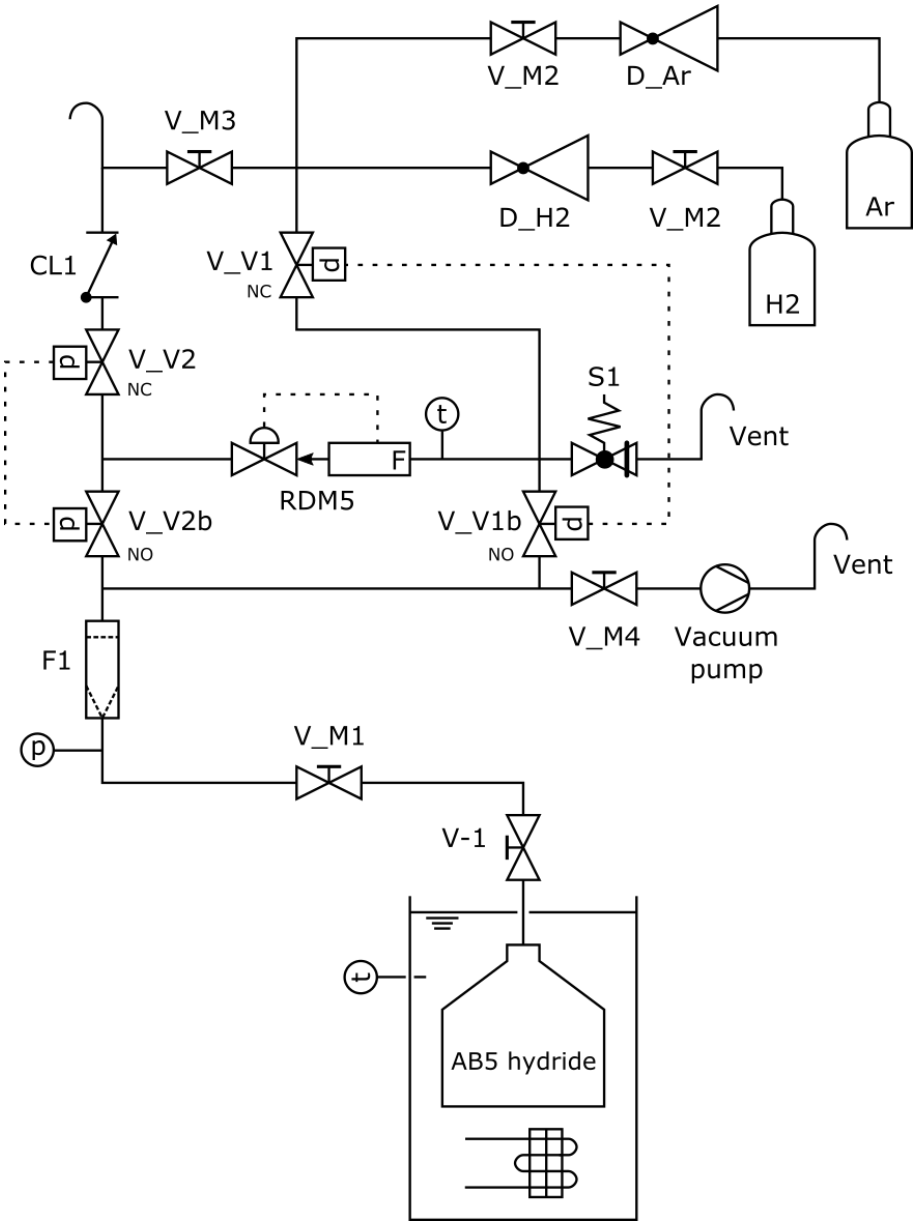

Figure 34 – P&ID diagram of the test bench at CEA-Liten.

Rig Employed Components:

Figure 34 shows the P&ID of the test bench at repose state (neither loading nor unloading hydrogen in tank containing hydrides). All components have been named for practical reasons.

Generally:

1. V_M_xx are manual valves
2. V_xx are piloted valves.
   Some are Normally Closed (NC), others are Normally Opened (NO)
3. Sxx are pressure release valves (pressure relief valves, safety valves)
4. Clxx are non-return valves (check valves)
5. D_xx are pressure reducers (pressure reducing valves)

In more detail:

1. Tubing: The circuit is constituted with 8-10 mm tubes (external diameter 10 mm, internal diameter: 8 mm). The fittings are two-ferrule fittings designed by Swagelok.
2. The pressure is measured by a pressure sensor DRUCK PTX 1400 (now GE sensing).
3. The temperature measurement is performed with thermocouple type K in stainless steel sheath.
4. The mass flow meter (RDM5) is a mass flow controller from Brooks (Distributor in France Serv'Instrumentation), model SLA5850S. It is equipped with a regulation valve that permits to directly control a desired mass flow. The regulation is done by an internal PID controller.

   Flow range 0 – 800 NmL/min @ 0 °C and 1 atm.
   Calibrated with He (450 mL) at 0.2, 6 and 12 barg and 21.10 °C by Serv'Instrumentation

   Accuracy (N_2 eq. at calibration conditions) given by the manufacturer:
   ±1.0 % of rate (20% - 100% full scale)
   ±0.2 % full scale (below 20 % full scale) up to 1100 L/min.
   (Optional: ± 0.7 % of rate ± 0.2 % full scale ("S-Series") up to 1100 L/min.

   Flow ranges above 1100 L/min and up to 2500 L/min ± 1.0 % of full scale (FS).

   Repeatability: ± 0.20 %;

   Temp sensitivity:
   Zero: less than 0.05 % FS per °C
   Span: less than 0.05 % FS per °C

   Pressure sensitivity:
   ± 0.03 % per psi up to 200 psig (N_2 eq.).

Pressure Differential Range (Controllers):

Minimum: 5 psi (0.35 bar) up to 30 L/min (N_2 eq.)
30 psi (2.07 bar) from 30 L/min to 50 L/min (N_2 eq.) with coplanar valve option

Maximum: with coplanar valve 250 psi (17-24 bar)

Minimum and maximum pressure drop: depends on gas and FS flow rate (consult factory).

Control Range

Turndown 50:1
Turndown 100:1 with coplanar valve option (for any FS range from 1-50 L/min (N_2 eq.))

Control Response

Settling time of less than 1 second

5. Vacuum pump: The vacuum pump is primary dry vacuum pump from Scroll Meister, model ISP250C: 15 m^3/h with ATEX capability (limit vacuum at the outlet: 1.6 10^{-2} mbar).
6. Metal hydride water bath: The water bath is a tap water bath.
7. Hydrogen: The hydrogen used to supply the test bench is hydrogen of quality 4.5 (99.995% vol. H_2). The pressure of the supply line is set to 12 barg.
8. Pilot valves: The pilot valves used for the test bench are diaphragm valves.
   V_V1 and V_V2: ROTAREX SELFA M8.1.5 316L PN240
   V_V1b and V_V2b: Swagelok SS-92S6MM-0
   V_M1 and V_M4: Swagelok ball valves SS-44S10MM

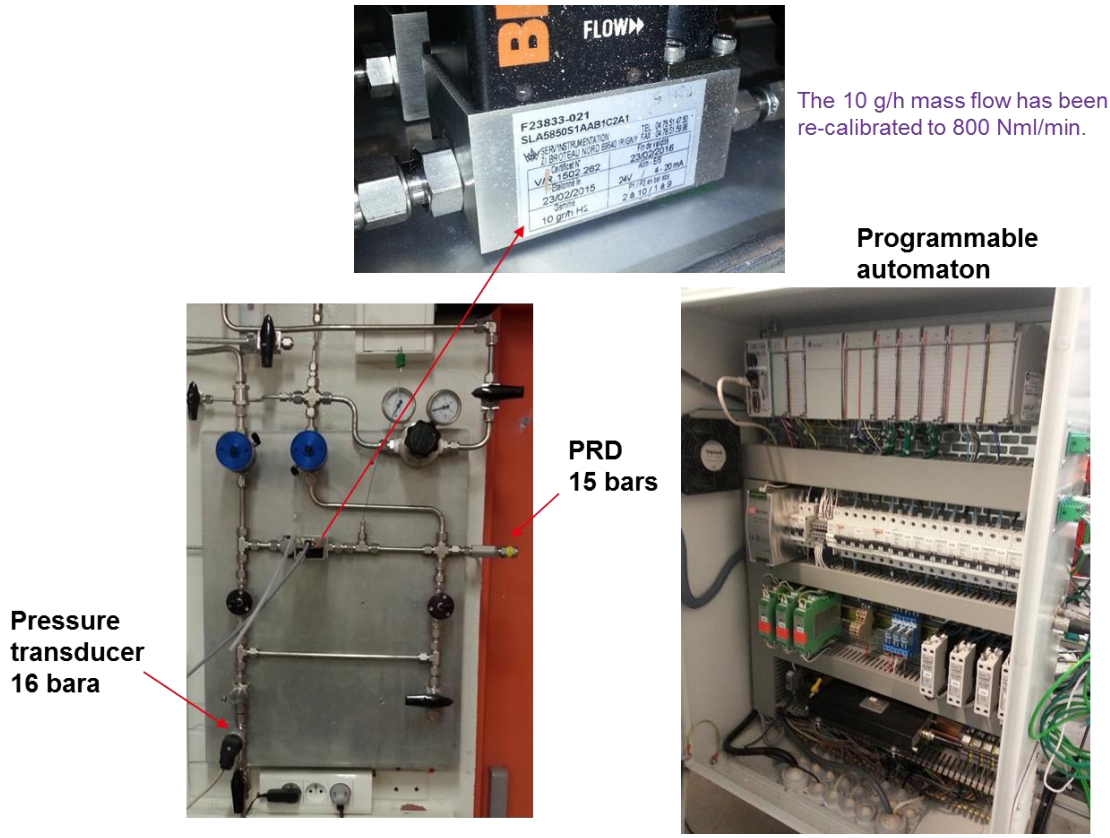

Figure 35 – Adapted test bench

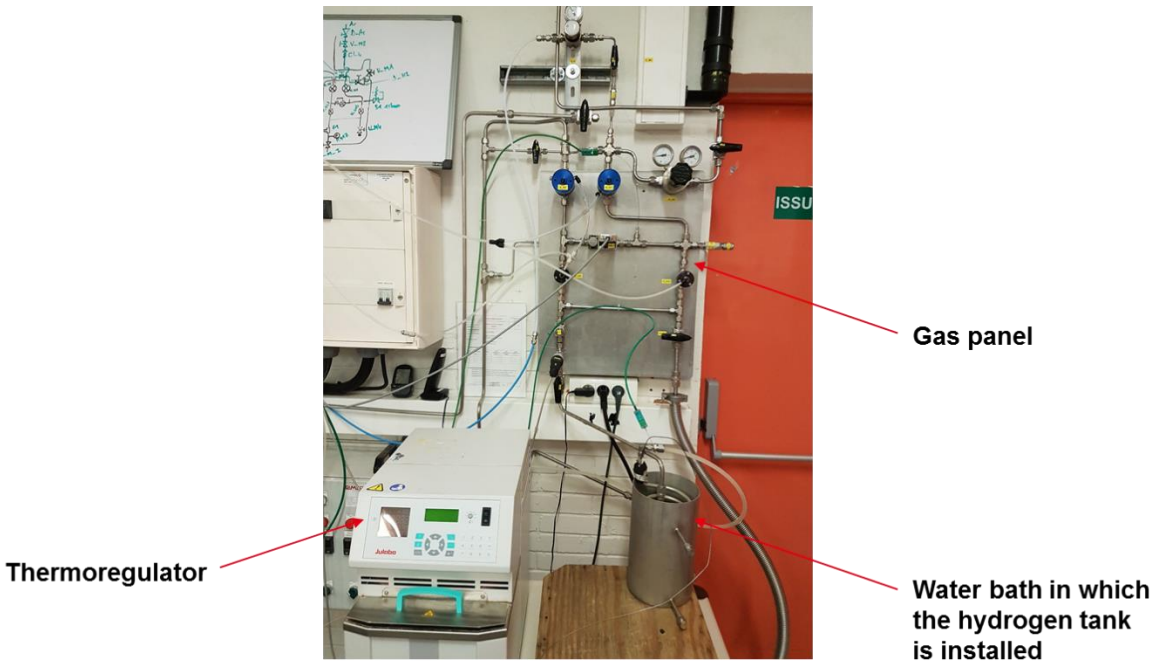

Figure 36 – Global view of the test bench at CEA-Liten.

Figure 37 – Piping system

Figure 38 – Photo of the thermocouple measuring the gas temperature at the entry of the mass flow meter (1 mm diameter thermocouple type K).

4.1.2 Working principle

This test bench is made around a BROOKS thermal mass flow meter and enables loading and unloading hydrogen in the tank with a maximum flow rate of 800 NmL/min between 0 to 15 bara.

For the purpose of the project, the test bench was modified from a previous one (see **Figure 37**). It has been simplified with only one mass flow meter, the length of the tube before the flow meter has been increased in order to improve the flowing condition before the mass flow meter. The temperature of the gas upstream the flow meter is measured by a thermocouple (type K) plunging inside the gas flow (see **Figure 38**), and the piping system has been improved (design) in order to have the possibility to easily choose between neutral gas (argon) and hydrogen. The test bench has been rendered more reliable by replacing the non-return valves to normal piloted valves, because we suspect non-return valves to allow some flow (leak) when used in the non-return function. We changed as well the Pressure Release Device (PRD) to 15 bars gauge (it was 12 bars).

In fact, the mass flow meter is also a mass flow controller, incorporating a progressive valve placed downstream of the flow rate measurement.

The test bench is controlled by an Allen Bradley automaton that guarantees a secured functioning and enables archiving data continuously to the Historian application that is really convenient for post-processing generated data. The test bench is piloted through an RSView interface. The interface has been adapted to the measurements. This interface enables to control valves separately or to launch the testing procedure and to plot different curves (evolution of the measurement data as a function of time mainly). The mass flow meter has been calibrated at Serv'Instrumentation.

<u>The circuit enables:</u>

- To measure the pressure inside the branch to the tank, this pressure can be considered to be the pressure inside the tank when the valves V_M_I and V_M_res are open. The pressure sensor has been recalibrated internally with a certified calibrated pressure sensor according to our internal quality scheme (ECME procedure).
- To measure the temperature of the gas just before the mass flow meter
- To measure the mass flow rate with the same instrument (named RDM5), by changing the state of the valves V_V1, V_V2, V_V1b, V_V2b.
    - V_V1b (resp. V_V2b) is normally open and is controlled at the same time of V_V1 (resp. V_V2)
    - **Figure 41** shows the configuration of the valves at loading or unloading hydrogen in the tank containing hydrides.
- To pump gas outside through a vacuum pump.
- To protect against powder pollution from the hydride tank with a F1 filter.
- To protect against overpressure with the PRD S1 target at 15 barg.

Temperature and heat control of the hydrogen hydride tank

Absorption or desorption of hydrogen is an exo-(endo)-thermic process. We chose to thermalize the tank at the same temperature for loading and unloading operations. The temperature of the tank, particularly inside the tank varies but the thermalized calo-carrier fluid will remain at the same temperature.

The temperature chosen for the calo-carrier fluid is T = 22 °C.

Technically, the tank is tempered by inserting it in a water bath (see **Figure 40**). The water is normal water from tap. The temperature of the bath is controlled by a thermoregulator. The water from the thermoregulator is not directly circulating around the tank (due to the way it is working). The water from the thermoregulator is circulating inside a helicoid closed circuit inserted in a water bath in which the tank is also plunged. In order to ensure a more homogeneous temperature in the water bath and a better heat exchange in the water bath, an agitator has been inserted.

Nota Bene: we have observed a strong corrosion on the screws closing the tank. This can be seen on the **Figure 40**. Although the corrosion effect is quite impressive, after removing it from the water bath, the traces are not so marked. There is some small stitching on the aluminium external vessel.

Figure 39 – Instrumentation of the tank. The thermocouple is installed under isolating neoprene foam, in order that the measure is closer to the temperature of the container wall than the temperature of the thermal fluid.

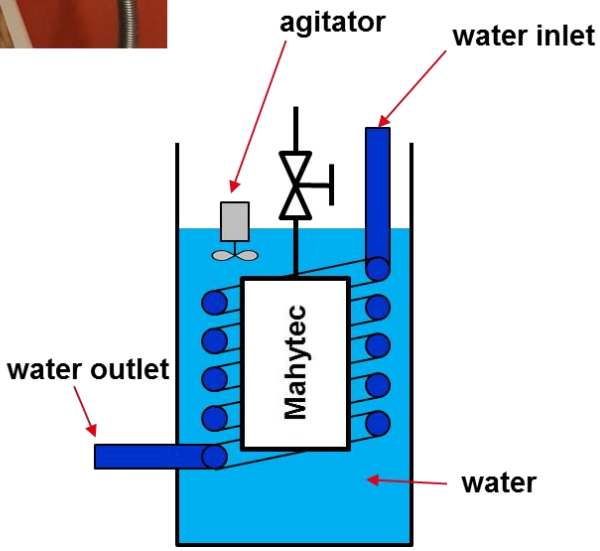

Figure 40 – Water bath inside which the tank is inserted.

4.1.3 Cycle testing

Starting procedure

For the beginning of the experiment, just after the sample has been mounted, the following procedure is applied:

1. Vacuum is done with:
    a. V_M4 opened (see **Figure 34**)
    b. V_V1 et V_V2 closed
    c. V_M_I opened
    d. V_M_res opened
    e. V_M1 is closed
2. V_M4 is closed and the circuit is filled by argon by opening V_M2. V_M2 is then closed
3. At this stage, we have done a cycling with hydrogen to test the automatic procedure while keeping V_M_res closed.
4. At the end, V_V1 is closed and vacuum is done by opening V_M4
5. V_M_res is thus opened very slowly in order not to vent too rapidly the tank
6. Vacuum during an hour. At the end V_M4 is closed.
7. The tank is now ready to absorb hydrogen and the cycling program can be launched.

Starting procedure (charge [load] and discharge [unload])

In order to have more reliable results, we have automatized the cycling of the tank (loading and unloading with hydrogen).

The programs as well as the conditions are given below:

Initial conditions		
P réservoir	-1	barg
T réservoir	22	°C
P H2 source	12.135	barg

Adjustable parameters			
RDM5 load	RDM5_load	400	Nml/min
RDM5 déload	RDM5_unload	400	Nml/min
Threshold for mass flow too low	SB_RDM5	2	Nml/min
Stability time	SB_tempo	60	s

Load	1	RDM5_C (RDM5 set point) = 0		
	2	Open V_V1		
	3	RDM5_C = 0,1		
	4	Wait : 5 s		
	5	RDM5_C = RDM5_load		
	6	Wait : 60 s		
	7	Close V_V1 when RDM5 < SB_RDM5 during more than SB_tempo		
	8	RDM5_C = 0		
Unload	9	Wait : 60 s		
	10	Ouverture V_V2		
	11	RDM5_C = 0,1		
	12	Wait : 5 s		
	13	RDM5_C = RDM5_unload		
	14	Wait : 60 s		
	15	Close V_V2 when RDM5 < SB_RDM5 during more than SB_tempo		
	16	RDM5_C = 0		
	17	Wait : 60 s		
	18	Back to step 2		

Note that in order to avoid an overshoot in the mass flow, we first set a very small set point to the mass flow controller (RDM5 = 0.1 NmL/min during 5 seconds).

The inlet pressure is adjusted by D_H_2 around 12 barg (13 bara), the measured pressure is 12.135 barg.

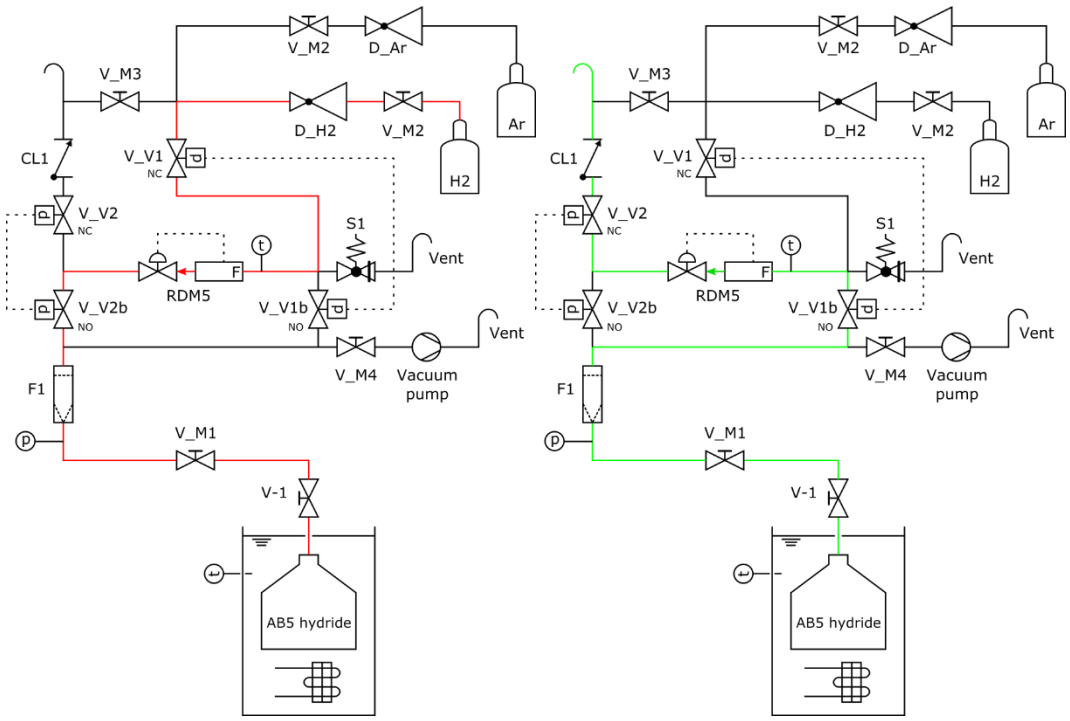

Figure 41 – left: load (charge); right: unload (discharge) configuration at CEA-Liten.

Corrections regarding dead volume

The circuit is made of large tubes and the volume of hydrogen in the tubes is significant compared to the volume of hydrogen that the tank can absorbed. This volume is counted by the mass flow meter, but it has not entered in the tank. This volume has to be withdrawn from the volume measured by the mass flow meter if we want to give as result the real capacity of the sole hydrogen hydride tank. This volume is evidenced on **Figure 42**.

The volume V1 is determined by:

1. closing the valve V-1
2. counting the quantity of gas passing through the mass flow and by the knowledge of the pressure.

The dead volume results in V1 = 75 mL.

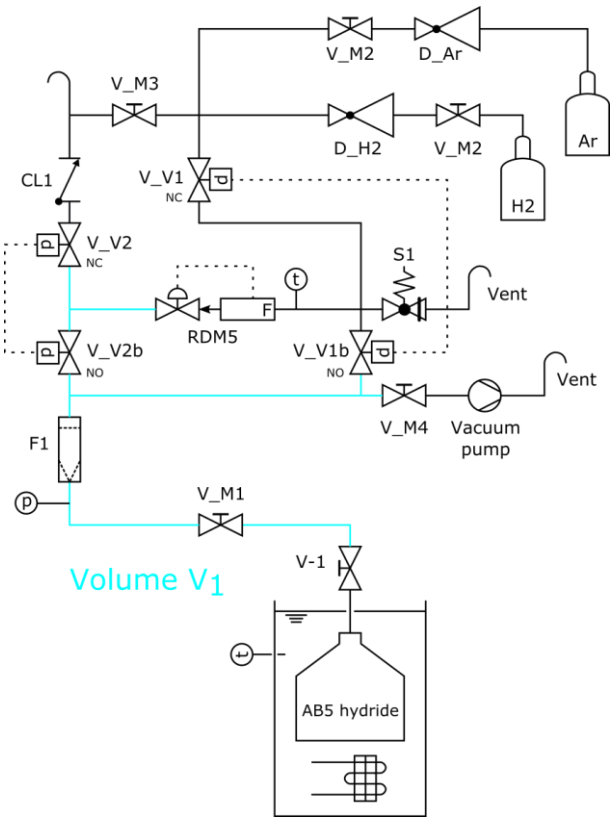

Figure 42 – Volume V_1 that has to be withdrawn from the real volume capacity of the tank.

4.1.4 Measurement results (AB5)

Experiment at 400 NmL/min

First cycle (re-activation)

Although the tank has already been activated at MAHYTEC premises, the first absorption was not direct. The result is shown on **Figure 43**. The mass flow is set to 400 NmL/min. The pressure starts from 0 bara and increases quite linearly. At a few minutes, the pressure drops suddenly. We relate this to the start of the real absorption of hydrogen by the hydride. At the same time, the temperature is increasing. The increase of temperature is very small (only 0.6°C) which seems not representative of the temperature increase in the hydride powder. This is explained by the fact that the aluminium vessel is highly heat conducting and that the measure of temperature is much closer to the temperature of the cooling water bath than to the temperature of the hydride. A thermocouple should be placed in the hydride directly to measure the temperature inside the tank.

At the same time, we can see that the mass flow rate is quite constant as long as the inlet pressure is far from the pressure inside the circuit close to the tank, but as soon as the maximum pressure is reached, the mass flow controller cannot sustain the desired flow rate, its regulation valve opens fully and the mass flow is thus used as a mass flow meter. After that, the mass flow drops quickly and it reaches under 4 NmL/min when a cut-off stops the measure. We consider the loading complete.

Then, after some temporization, the unloading begins. We can see that the pressure drops very quickly, and a large part of the unloading is taking place with a low pressure. At the same time, the temperature exhibits a small decrease witnessing the endothermicity of the desorption reaction in the hydride.

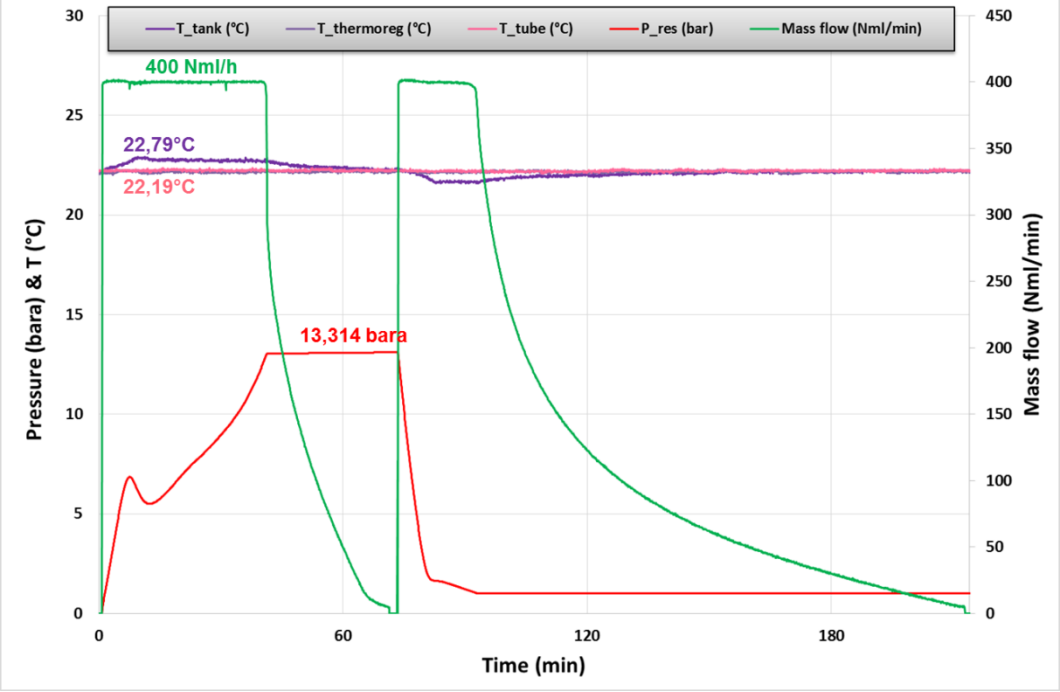

Figure 43 – Measures during the first absorption of the tank at 400 NmL/in flow rate.

Other cycles

After the first cycle, all the others are quite stabilized. The 5th cycle is presented on **Figure 44**. It can be seen that the pressure increase during the loading phase has a particular shape. In fact, this shape

is related to the shape of the PCT equilibrium curve of the material, with a shift because the temperature in the tank is higher.

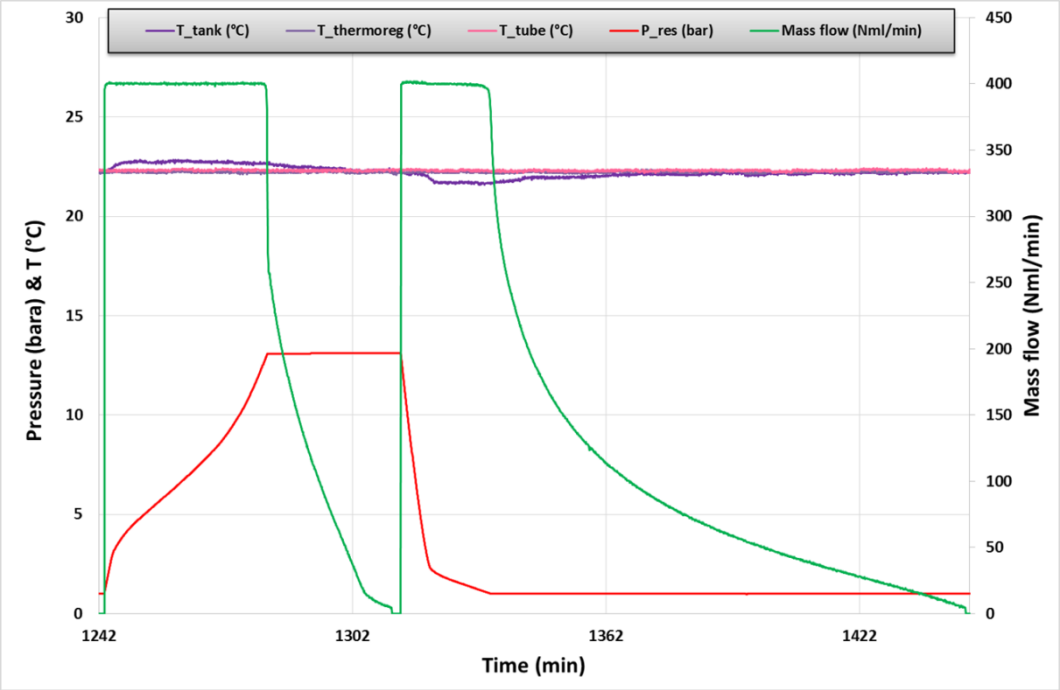

Figure 44 – 5th cycle at 400 NmL/min flow rate..

Volume calculation

The volume absorbed by the tank is calculated from the measurements by integrating the flow rate over time and doing the volume correction explained on page 46.

Cycle after cycle, it appears quite evidently that there is a shift in the absorbed volume. This shift can come from two causes:

1. The material is absorbing more and more hydrogen

Note that this is the case in between the first cycle and the second cycle, because the first cycle begins at p = 0 bara, whereas it ends, after desorption, at p = 1 bara. This is evidenced on **Figure 46**, which clearly exhibits a higher volume absorbed for the first cycle.

2. The measure is not accurate

We note that after the first absorption, the absorbed and desorbed volumes seem not to increase. In fact, the increase of the integrated volume in the tank comes from the fact that the absorbed volume is always greater than the desorbed volume. For the first cycle, it has already been explained, but it is less understandable for the other cycles, knowing that for each cycle, pressure and temperature are coming back very closely to the same values. This kind of disequilibrium between the absorption and desorption should diminish in a very few cycles.

This is consolidated by the fact that the absorbed capacity is very close to the theoretical capacity of the tank.

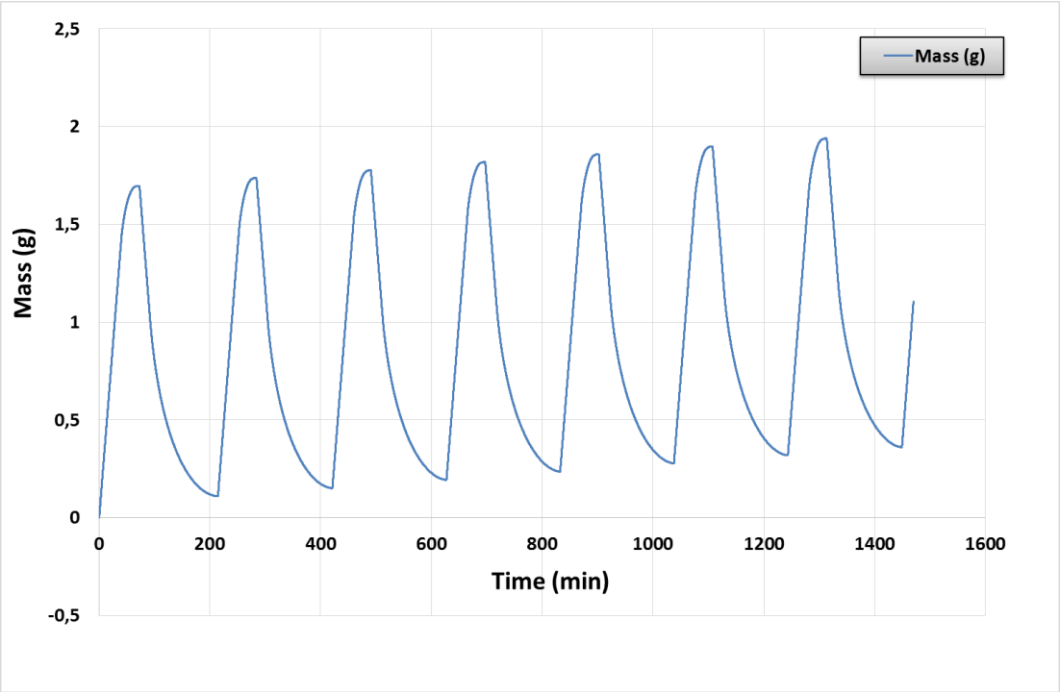

Figure 45 – Absorbed volume in the tank for the test at 400 NmL/min.

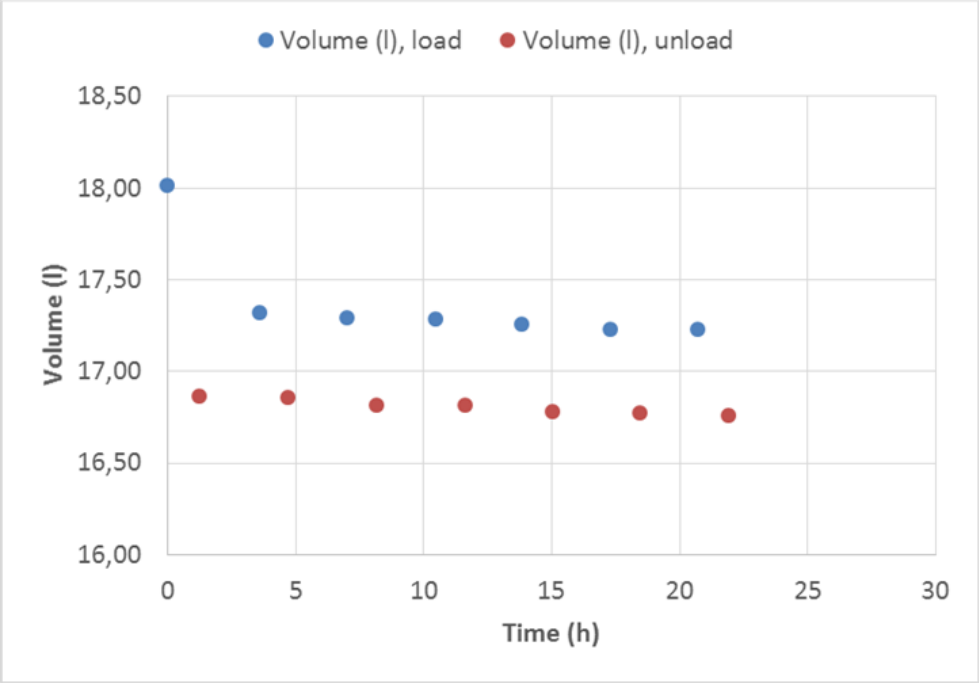

Figure 46 – Absorbed volume in the tank for the test at 400 NmL/min, total for each absorption and desorption.

Mean deviation per cycle = 0.47 L ⟶ 2.79% (unload)
Mean absorbed volume = 17.27 NL = 1.54 g
Mean desorbed volume = 16.80 NL = 1.50 g

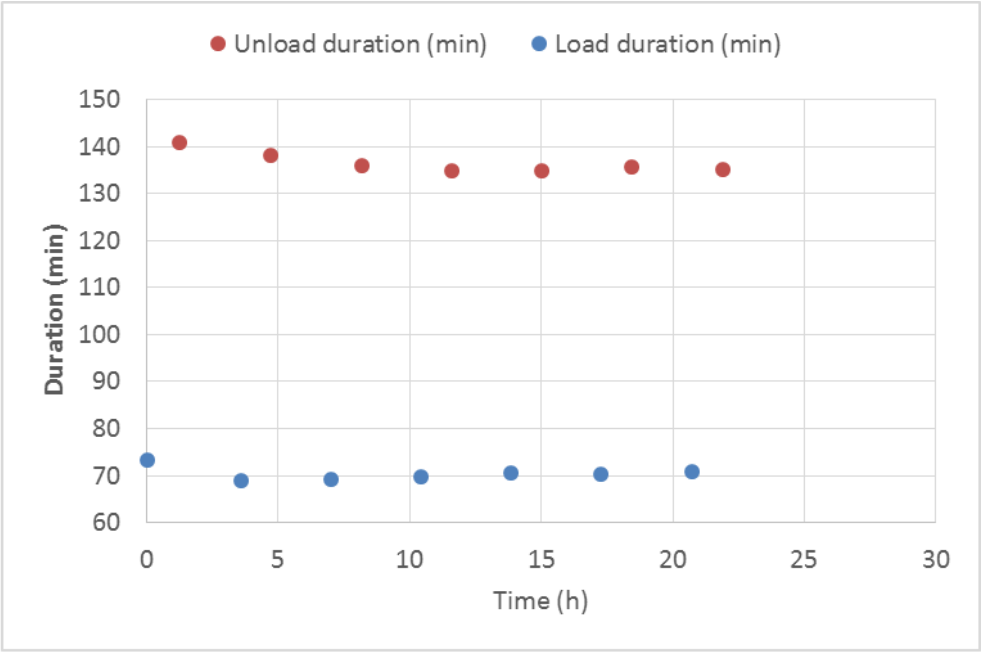

Figure 47 – Loading and unloading times for the test at 400 NmL/min. The mean cycle duration is 206 min (=3.44 h).

Experiment at 100 NmL/min and 50 NmL/min

Two other flow rate conditions have been imposed to the tank after the first one at 400 NmL/min (100 NmL/min and 50 NmL/min).

The results are given in **Figure 48** and **Figure 49**.

During these tests, the flow rate is smaller, and the duration of the phase of the loading or unloading when the mass flow rate can be maintained at the desired value is increased.

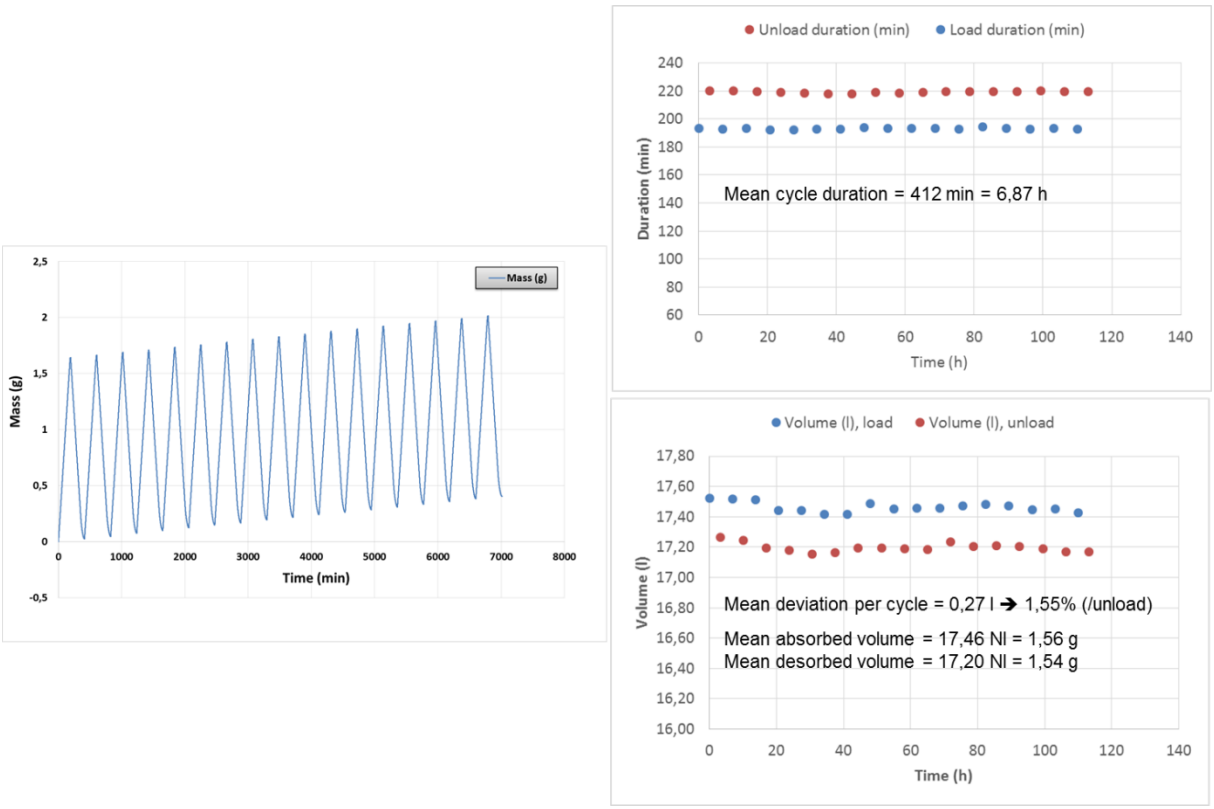

Figure 48 – Measurement results for the tests at 100 NmL/min.

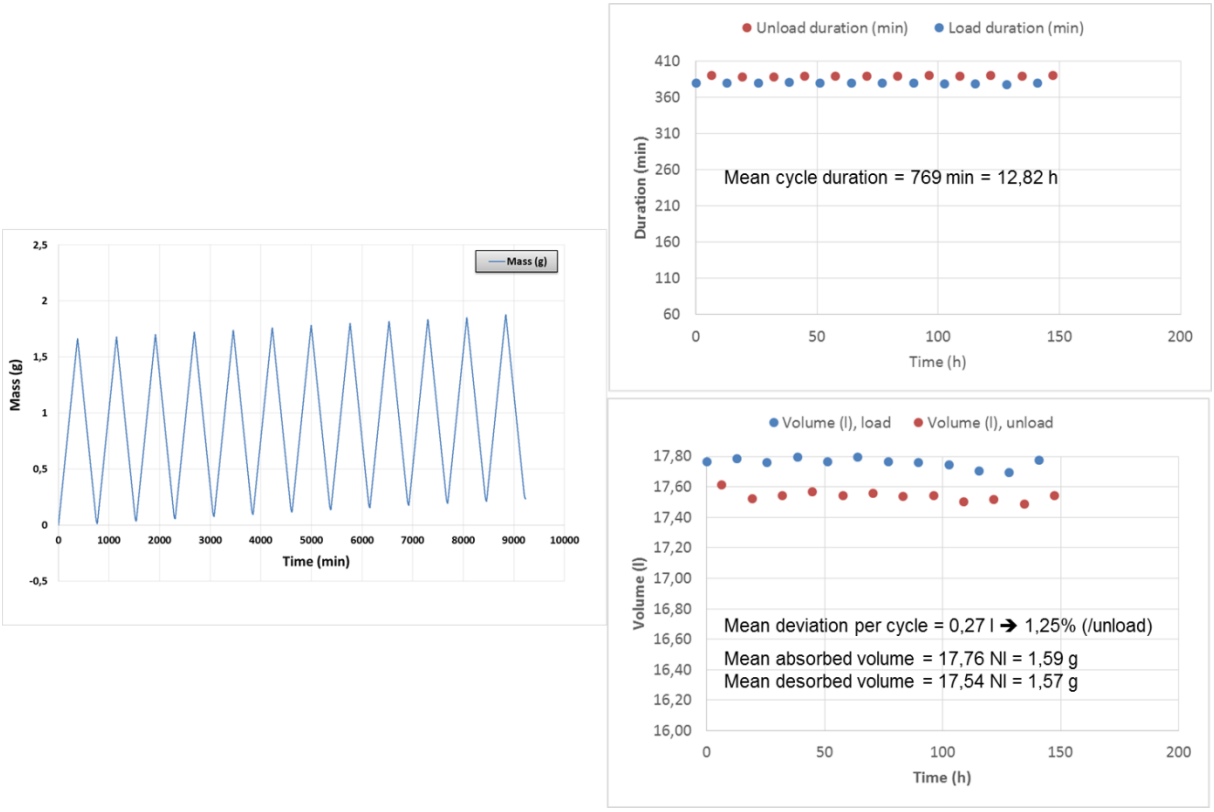

Figure 49 – Measurement results for the tests at 50 NmL/min.

Comparison of the three flow rate conditions

Table 4 presents a comparison of volumes, durations and deviations for the three different mass flow rates. The results are also plotted in **Figure 51**.

Table 4 – Compilation of the results for measurements at different flow conditions.

Mass flow	t load	t unload	V load	V unload	Deviation	MAHYTEC capacity	Difference to announced capacity (load)	Difference to announced capacity (unload)
NmL/min	min	min	NL	NL		NL		
50	379.71	389.59	17.76	17.54	1.25%	16.80	5.71%	4.40%
100	193.17	219.27	17.46	17.20	1.55%	16.80	3.93%	2.38%
400	69.92	136.46	17.27	16.80	2.79%	16.80	2.80%	0.00%

It can be seen that higher is the flow rate, the lower is the loading time or unloading time. But, there is limitation due to heat transfer in the hydride, and the law is far from linear. Increasing the flow rate in order to fill quickly the tank is less and less beneficial (it is still increasing the kinetic, but slowly).

Concerning the absorbed or desorbed volumes, if high mass flow rate is chosen, the total volume of absorbed H_2 is decreasing (2.8 % less when passing from 50 NmL/min to 400 NmL/min).

Besides, the deviation of volume between loading and unloading increases when the imposed flow rate increases. This has to be explained and will be discussed in **section 4.1.5** but we can remark that if the chosen imposed flow rate is lower, the mass flow meter works in a better condition during a longer time than if the mass flow rate is higher.

It should be noted that the maximum ratio (dynamic range) of a typical thermal mass flow meter or mass flow controller is around 1:20. When the flowmeter has a nominal flow rate of 400 NmL/min, the minimum flow rate should not be lower than 20 NmL/min (5 % of the nominal flow rate). In case measurements will be performed down to 4 NmL/min (1 % scale) a large measurement deviation can be expected from the flow meter.

In general, the measurement accuracy of a “good” flow meter should be conservatively estimated with 2 % for the measurement range of 1:20.

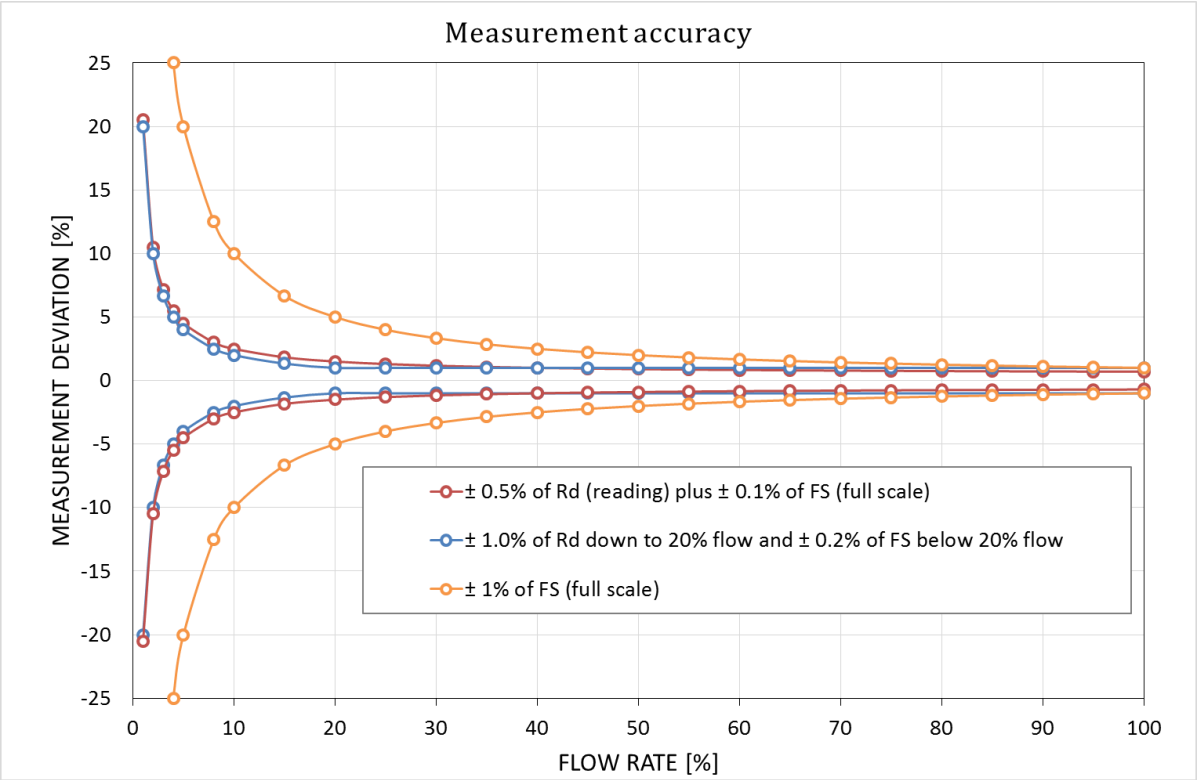

Figure 50 – Typical measurement accuracy of a mass flow meter or mass flow controller.

Figure 50 shows three (typical) measurement accuracies for mass flow meters and/or mass flow controllers:

a) ± 0.5 % of Rd (reading) plus ± 0.1 % of FS (full scale)
b) ± 1.0 % of Rd (reading) down to 20 % flow and ± 0.2% of FS (full scale) below 20 % flow
c) ± 1.0 % of FS (full scale)

The information regarding the accuracy measurement of the flow meter can usually be found in the manual guide.

Compared to the capacity announced by MAHYTEC, the measured values (volume for instance) are quite in agreement. Note that our value is the capacity of the tank when loaded with hydrogen with a pressure of around 13 bara, including the gas part in the porosity and in the free volume of the tank. Knowing the value of the free volume in the tank (porosity and spare volume not occupied by the hydride powder) could allow us to calculate the real part of H_2 absorbed in the hydride powder.

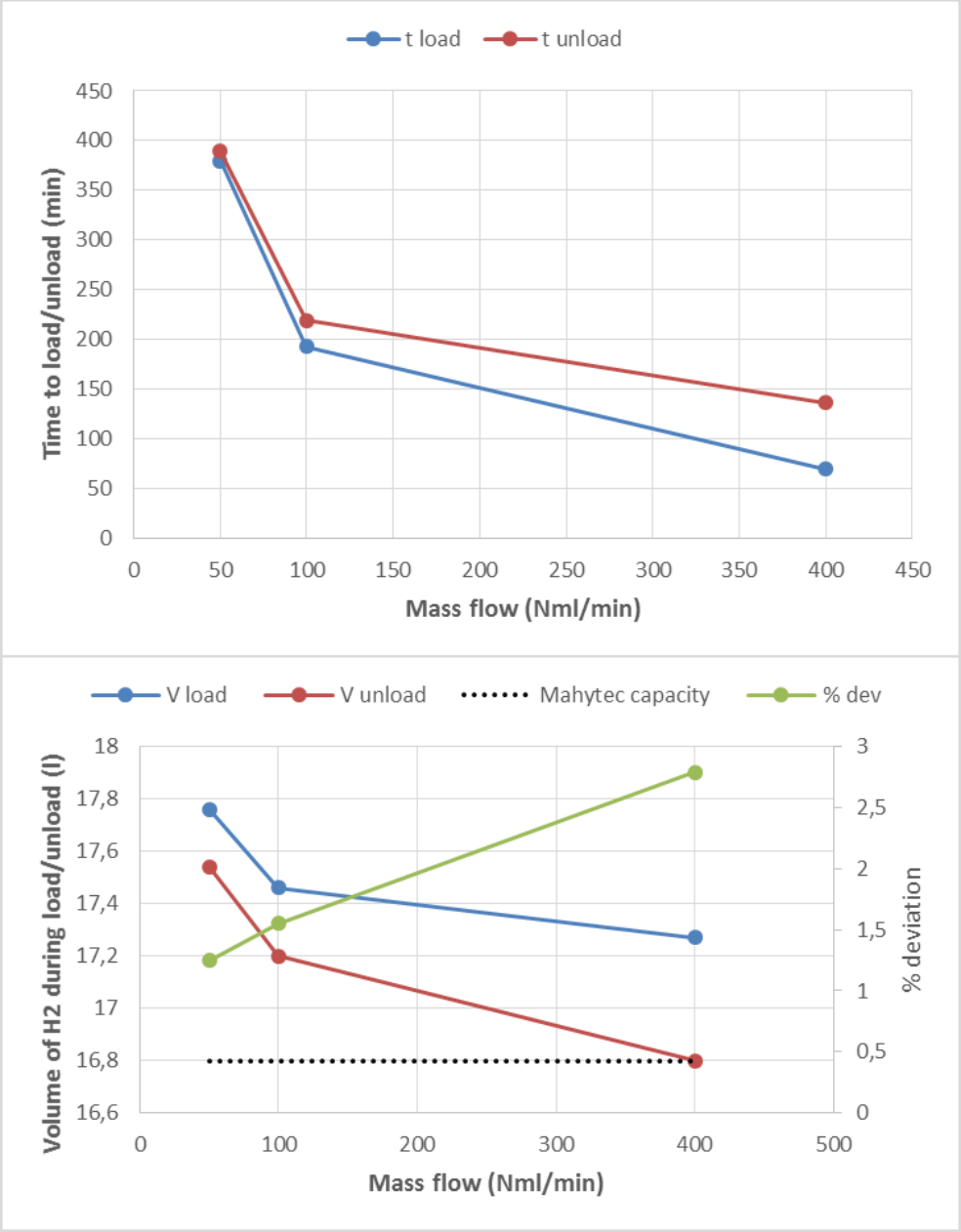

Figure 51 – Comparison of volumes, durations and deviations for different mass flow rates.

Possible influences on the measurement accuracy of the flow meter

Corrections regarding measurements at low pressure

In this part we propose to explore the behaviour of the mass flow controller at Serv' Instrumentation with a deviation observed at low pressures.

Flowmeter calibration at Serv' Instrumentation

A scheme of the measure device used for the calibration operation is given in **Figure 52**. It is composed of a certified calibrated volumeter, made of a mobile piston in a closed chamber. The measure of the displacement of the piston during a certain time enables the measurement of the volumetric flow rate coming from the thermal mass flowmeter installed upward the gas circulation. A pressure regulator placed upward the thermal mas flow meter is used to regulate the pressure in the mass flow meter. A pressure regulator placed after is used to adjust the pressure at the outlet of the thermal mass flow meter.

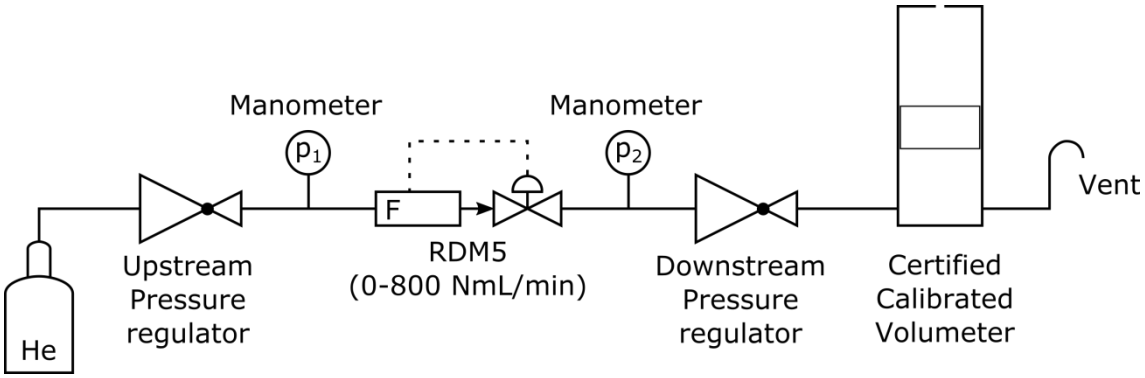

Figure 52 – Calibration apparatus at Serv' Instrumentation.

The calibration of the thermal mass flow meter RDM5 has been carried out at P_1 = 6 bar and $P_2 = P_{atm}$ (atmospheric pressure plus some small pressure losses). Thereafter some complementary measurements have been performed at P1 = 0.2 bar and P1 = 12 bar, with $P_2 = P_{atm}$ in both cases.

The calibration results are presented on the next pages.

Correction principle

The working conditions of the mass flow controller are summarized in **Table 5**. Besides, it has been observed a deviation when the pressure P_{in} is low. This is summarized on Figure **53**. We can see that the deviation is quite important at low P_{in} pressure (when P_{out}=atmospheric pressure).

Table 5 – Working conditions of the mass flow controller.

	P_{in} (bara)	P_{out} (bara)
Loading (charge)	13.136	P_{tank}
Unloading (discharge)	P_{tank}	0.985

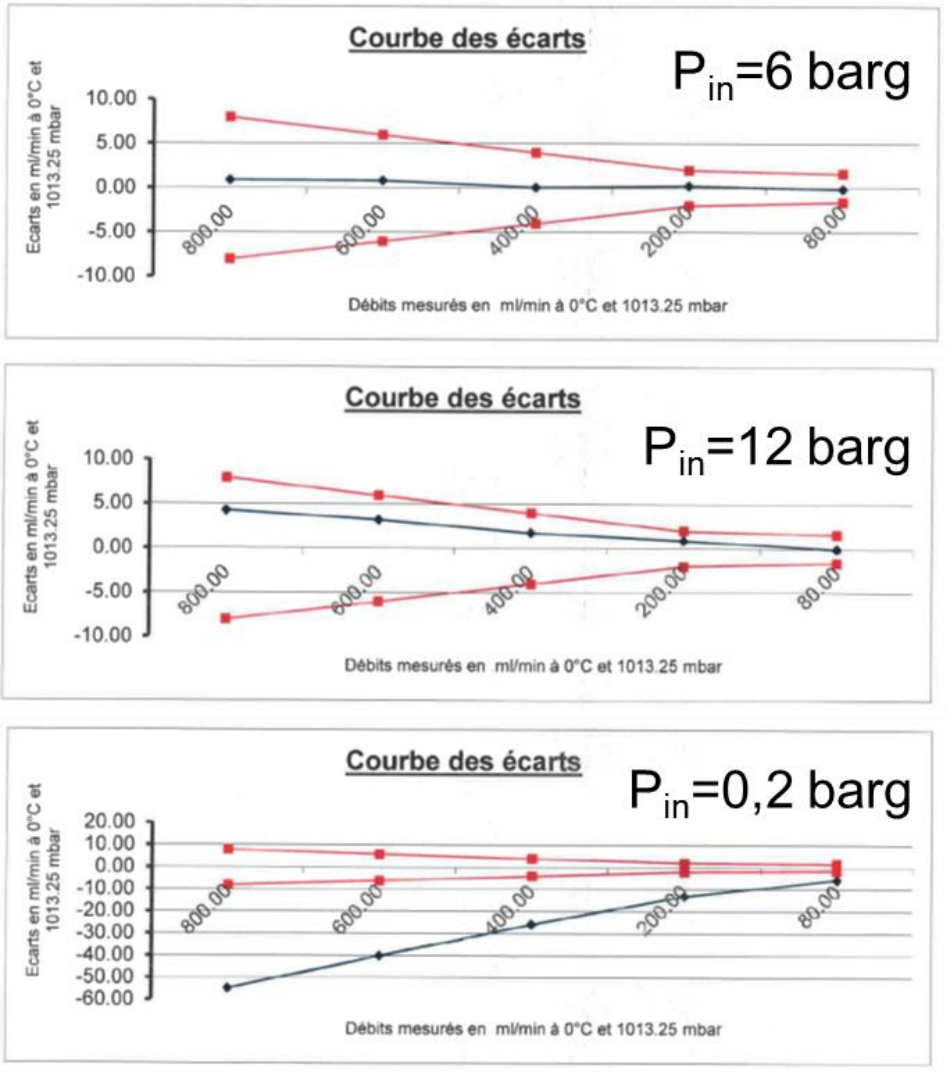

Figure 53 – Record of the deviation for several inlet pressures P_{in} (0.2, 6 and 12 barg). P_{out} = atmospheric pressure.

Table 6 – Calibration measurements at different pressures at Serv' Instrumentation.

Pressure	Reference flow mL/min	Measured flow mL/min	Output signal mA	Difference mL/min	Uncertainty mL/min	Maximum theo. uncert. mL/min
6 bar	799.10	800.00	20.00	0.90	4.40	8.00
	599.18	600.00	16.00	0.82	3.30	6.00
	399.94	400.00	12.00	0.06	2.20	4.00
	199.77	200.00	8.00	0.23	1.10	2.00
	80.15	80.00	5.60	-0.15	0.44	1.60
12 bar	795.73	800.00	20.00	4.27	4.38	8.00
	596.79	600.00	16.00	3.21	3.28	6.00
	398.25	400.00	12.00	1.75	2.19	4.00
	199.11	200.00	8.00	0.89	1.10	2.00
	80.06	80.00	5.60	-0.06	0.44	1.60
0.2 bar	854.74	800.00	20.00	-54.75	4.70	8.00
	640.05	600.00	16.00	-40.05	3.52	6.00
	425.81	400.00	12.00	-25.81	2.34	4.00
	213.07	200.00	8.00	-13.07	1.17	2.00
	85.70	80.00	5.60	-5.70	0.47	1.60

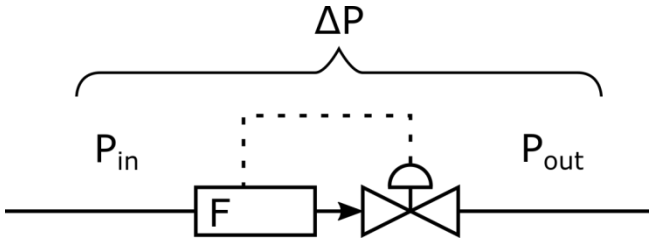

Figure 54 – Inlet pressure, outlet pressure and differential pressure.

In order to test what would be improved to consider the deviation at low pressure, a fit has been adjusted to represent the observed behaviour. It is given on **Figure 55**.

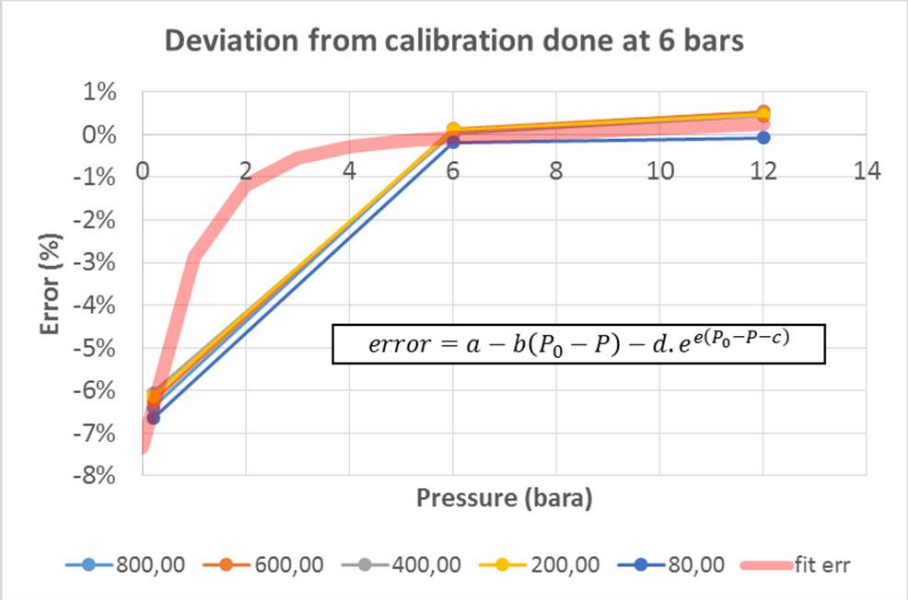

Figure 55 – A fit have been adjusted to represent the deviation behaviour.

Application of the correction to the results at 400 NmL/min

Figure 56 and **Figure 57** present the effect on the correction proposed in the previous part.

With the correction, the deviation observed on the absorbed mass is decreased (-1.21 %) compared to the deviation before the correction (2.79 %). With no correction, the total absorbed mass increases, whereas with the correction, it decreases with a smaller effect.

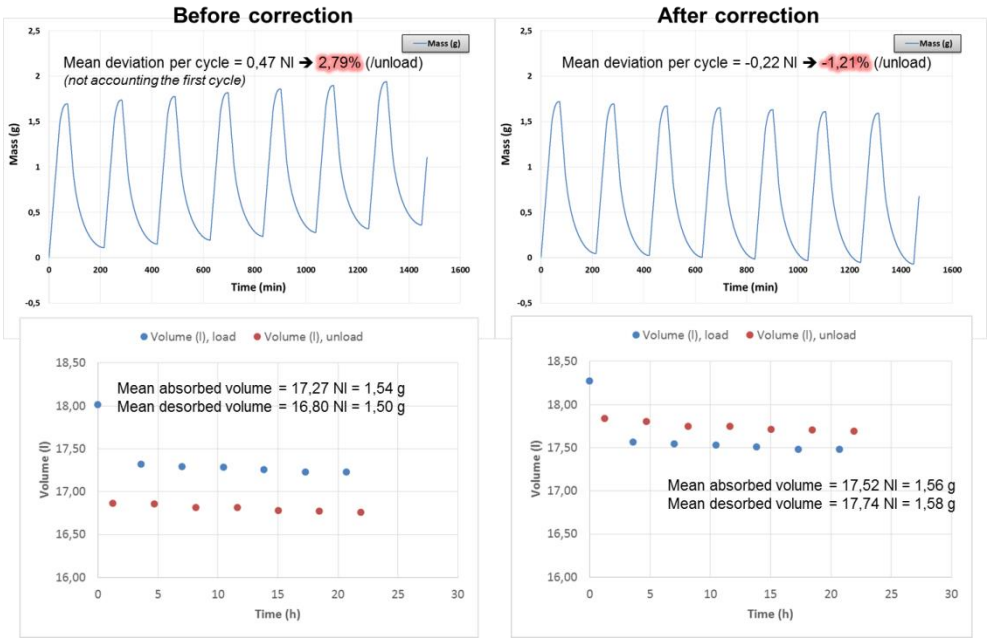

Figure 56 – Effect of a correction with the equation fitted in part 3.4.1 for a mass flow rate of 400 NmL/min. Effect on absorbed mass and volume.

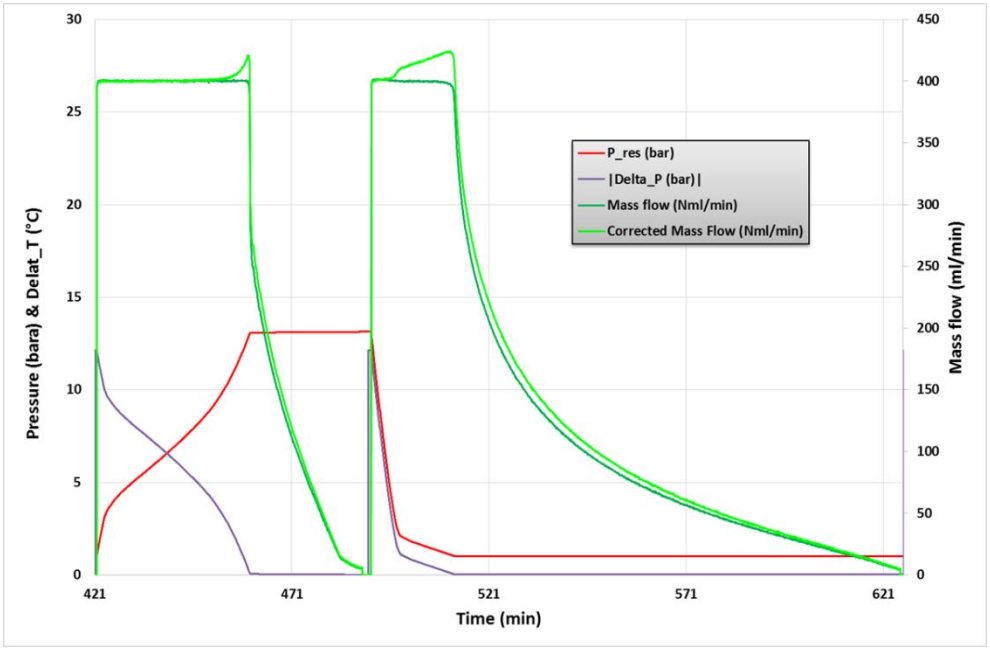

Figure 57 – Visualization of the correction with the fitting equation in section 0 for a mass flow rate of 400 NmL/min. Effect on the measured flow rate on the 5th cycle.

Application of the correction to the results at 100 NmL/min

Figure 58 and **Figure 59** present the effect on the correction proposed in the previous part.

In that case, it is observed that the applied correction has the same behaviour but with a higher negative deviation (-1.96 %). This means that:

1. The correction is not well evaluated
2. The deviation that this correction aims at reducing is not the only type of deviation happening when doing the measurement.

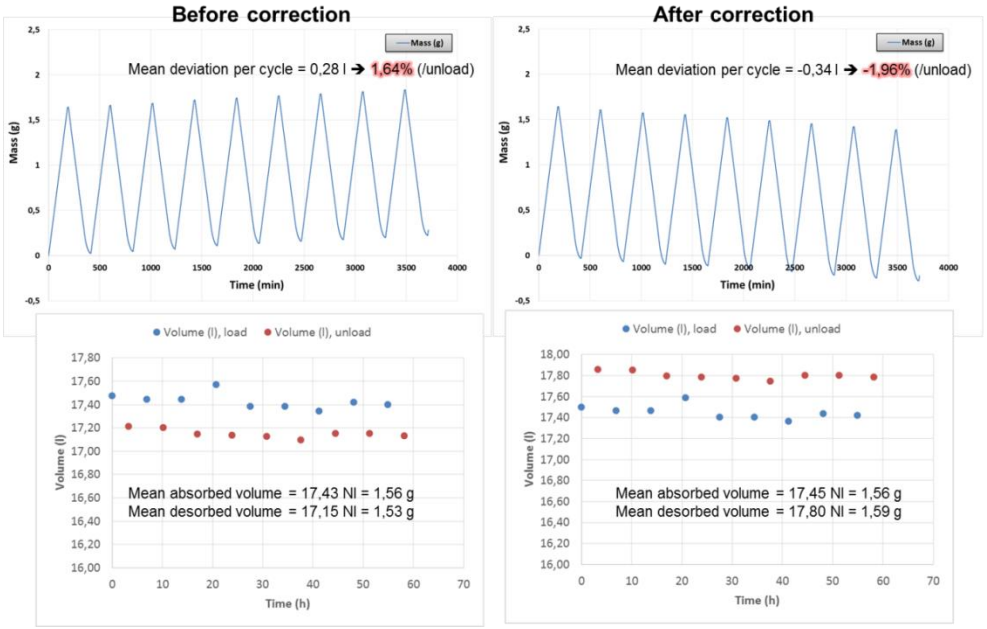

Figure 58 – Effect of a correction with the equation fitted in section 0 for a mass flow rate of 100 NmL/min. Effect on absorbed mass and volume.

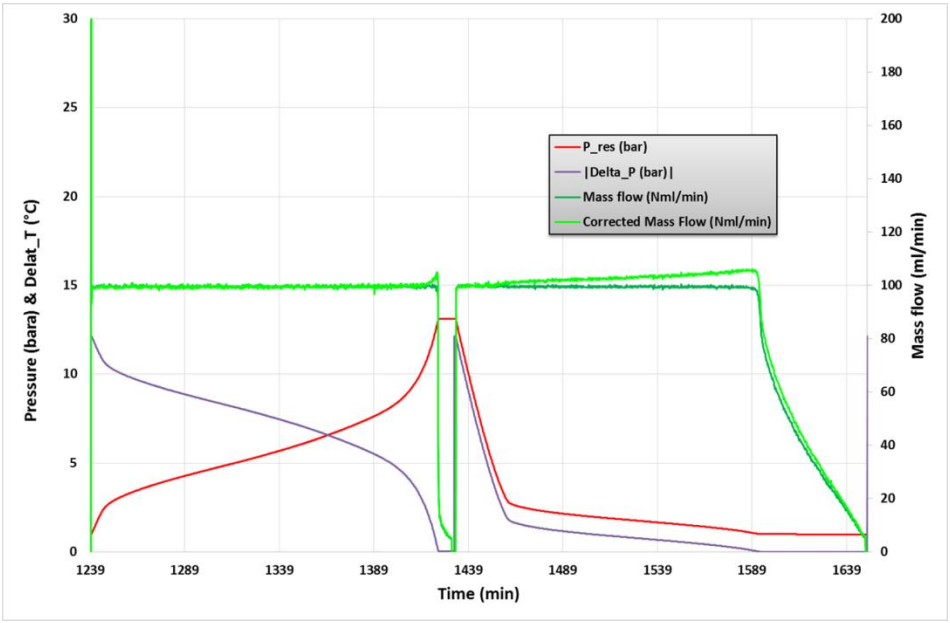

Figure 59 – Visualization of the correction with the fitting equation in section 0 for a mass flow rate of 100 NmL/min. Effect on the measured flow rate for the 4th cycle.

Implementation of a 'perfect fit' method for the correction of the volume

A non-physical correction method is presented here that reduces the volume deviation to a minimum value.

The law to fit the experimental calibration results of the mass flow rate is assumed to take place only for very small ΔP: for $\Delta P < \Delta P_{threshold}$ the error on the measured flow rate is assumed to be 7 % greater than the read value (see **Figure 60**).

This is not really physical and proven, but this is done to assess whether we can find a correction curve that annihilates the deviation and what this curve looks like.

Apparently, when $\Delta P_{threshold}$ = 0.35 bara, the deviation is quite reduced (**Figure 61** and **Figure 62**).

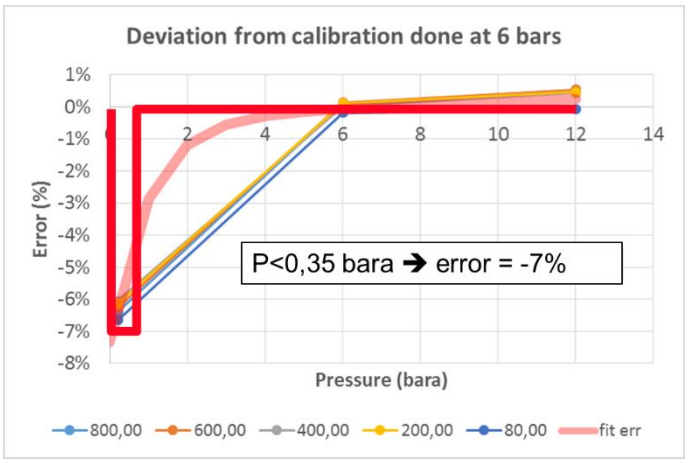

Figure 60 – A fit have been adjusted to represent the deviation behaviour.

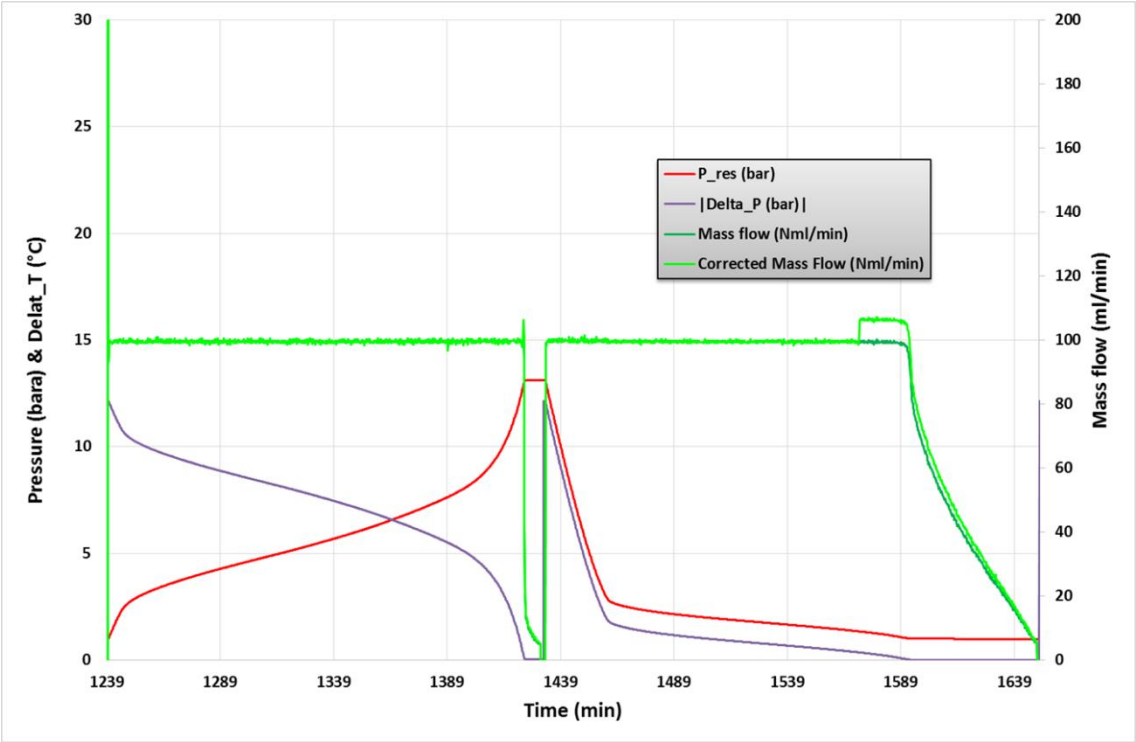

Figure 61 – Visualization of the correction with the equation fitted in this appendix for a mass flow rate of 100 NmL/min. Effect on the measured flow rate for the 4th cycle.

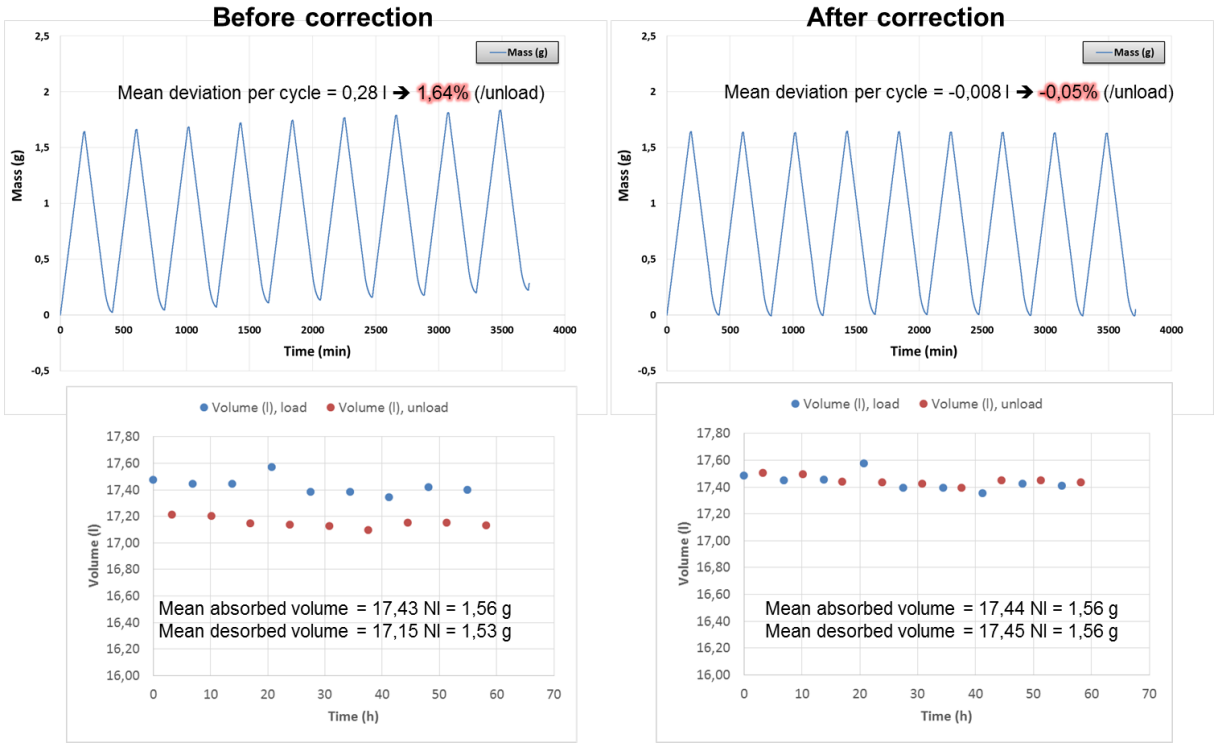

Figure 62 – Effect of a correction with the equation fitted in this appendix for a mass flow rate of 100 NmL/min. Effect on absorbed mass and volume.

Complementary results on the deviation recorded of the mass flow controller

Some complementary results on the mass flow controller calibration have been obtained. Additional points are here observed for low ΔP between 0.2 and 6 barg. The results are presented in **Figure 63**.

The deviation is even worse than what was expected.

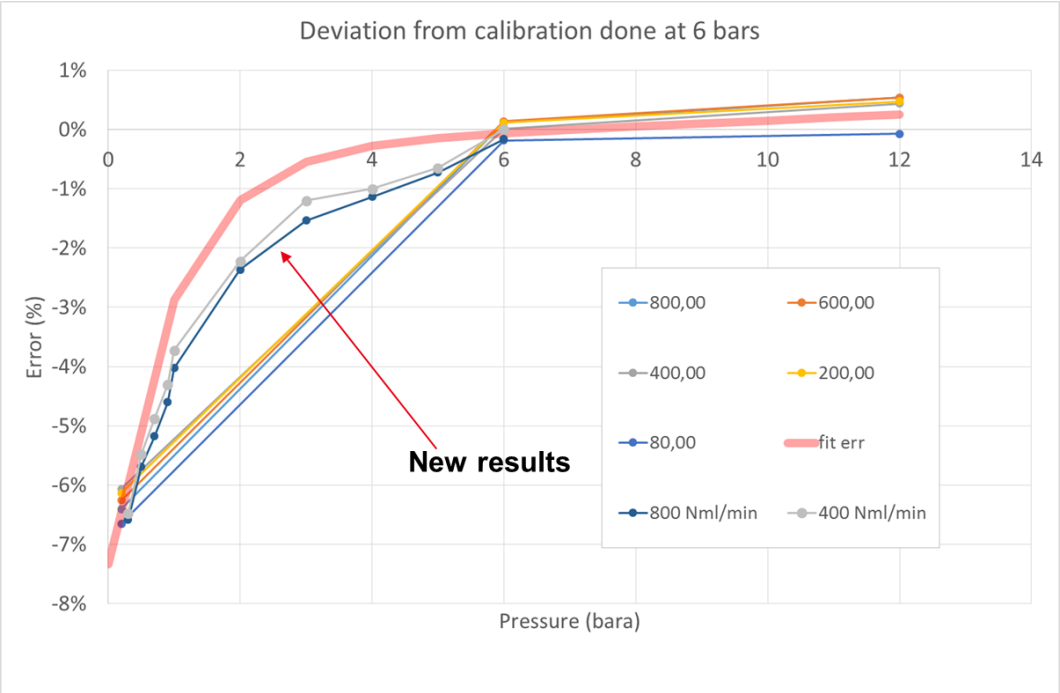

Figure 63 – Results of complementary calibration point done between 0.2 and 6 barg.

4.1.5 Discussion after the tests with AB5

Three mass flow conditions have been tested on the hydride tank provided by MAHYTEC: 400 NmL/min, 100 NmL/min and 50 NmL/min.

The measured mass (or volume) capacity of the tank is in agreement with the capacity announced by MAHYTEC (1.5 g = 16.8 NL H_2). The errors on the capacity measurements are from 0.00% to 5.71%.

A remained issue has to be highlighted: during cycling, a deviation in the global volume of hydrogen absorbed and desorbed by the tank is still observed. Non-negligible hydrogen mass remains in the tank with increasing the cycles under the same loading and unloading conditions. According to physics of hydrides, we have concluded that this phenomenon is to be preferably linked to a deviation in the mass flow rate measurement.

The deviation observed is more than the maximum error given by the mass flowmeter manufacturer for the mass flowmeter rates used on the test bench.

The deviation is more pronounced with higher flow rates.

When submitting the mass flow controller to an extended calibration procedure, we have recorded that the mass flow controller is well calibrated above the value at which it was calibrated, but it gives underestimated values when working at lower inlet pressure (with atmospheric pressure at the outlet).

We have tried to do correction with this information. For some conditions, the correction is decreasing the volume deviation explained above, but for some other conditions (low flow rate), the deviation from corrected results is reversed and even worse than without correction.

<u>This could mean that:</u>

A. The correction is not well evaluated

B. The deviation that this correction aims at reducing is not the only type of deviation happening when doing the measurement.

Even if we have underlined a calibration issue, we have not explained from where the observed deviation in absorbed volume is coming from. Some explanations can be argued as:

- The calibration procedure and/or apparatus could create the calibration deviation observed for low values of ΔP. The mass flow is used as a mass flow controller; it is adjusting the valve aperture to ensure the desired mass flow. Can this have an influence on the measure? Influence by flow fluctuations, influence by thermal effect. Proposed thing to be done :
    - Use the mass flow controller as a mass flow meter solely, inhibiting the command of the valve. The best would be to remove the valve in order to avoid the heating if we maintained the valve opened
- Conversely, the mass flow controller when used in the situation of a low ΔP is in the fully opened valve situation. In this position, the valve electrical actuator is fully powered, it is thus heating. We have suspicion that this heat has an influence on the measure. It is highly unlikely if we consider that this heating takes place after the measuring sensor as the valve is located downstream the sensor. Proposed thing to be done:
    - Same a previous point. Use the mass flow as a mass flow meter solely: remove the valve.

- The deviation may also come from the test bench itself. V2 volume is not accounted by the flow meter during the unloading phase. Conversely, V3 volume is accounted by the flow meter during the unloading phase although it is not hydrogen coming from the tank. We did correction by the major “lost” volumes that are not measured during the procedure (see **Figure 64** below).

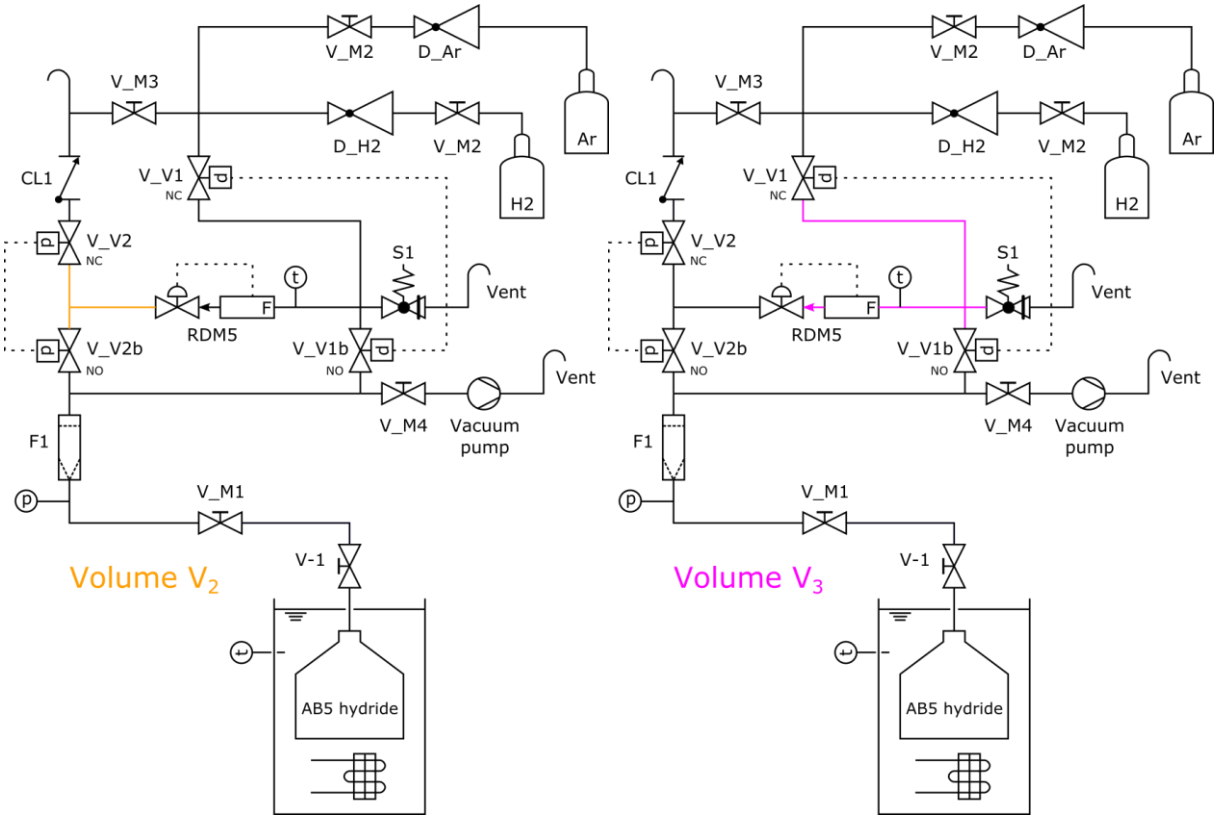

Figure 64 – Lost volume and added volume during unloading.

- Proposed thing to do:
    - Try to evaluate more accurately the influence of supplementary corrections.
- We have observed that when the mass flow controller is opening, it is first opening with a high aperture for a very brief time (even though we have adopted a special procedure asking the mass flow controller to aim at a very small flow rate before asking for a higher flow rate). We have supposed that it created a negligible deviation, by estimating the volume lost by the measure of the flow peak recorded by the mass flow when this occurs. But we are not sure that the measured value is good and that the signal of the flow rate is well integrated over time during this peak flow. Things to be done:
    - Try to intensify the time integration during these peak event
    - Try to estimate more accurately the error coming from this phenomenon.
- There may be as well a problem of time integration of the flow rate during transient flow regimes. Things to be done:
    - Try to estimate this error

- The mass flow meter is maybe doing its proper time integration internally. Try to access this value and compare it to the post-treatment time integration.

- There may be as well error coming from the fact that the mass flow meter is calibrated with Helium and that measurements are taking place with hydrogen. Thing to be done:
  - Check thermal properties of each gas (density, heat capacity, conductivity) and deviation with pressure (heat capacity has a strong influence on mass flow measurement by thermal methods).

All these have to be explored more thoroughly.

4.2 Measurements with AB

4.2.1 First AB tank

The initial plan was that each partner will carry out measurements with an AB-type tank after the measurements with the AB5 type tank have been completed. For this reason, every partner returned the AB5-tank to MAHYTEC and MAHYTEC changed the AB5 hydride in the tank with an AB type hydride (see section 2.4.1). .

For unknown reasons, CEA-Liten obtained no detectable absorption in the hydride with the tank provided by MAHYTEC.

4.2.2 Second AB tank

CEA-Liten has received (as second AB tank) the AB tank from FHA. This tank has been successfully tested at FHA. The received tank was sealed tight by a Swagelok plug as well as V_M_res closed.

Apparently, although CEA-Liten took all the caution to connect the tank to the test bench, the tank did not activate in the sense that it could not be observed temperature variation on the wall of the tank, and that the admitted hydrogen quantity in the tank only corresponds to the filling of the void space in the tube and the tank.

A pressure test (leak test) has been realized. The pressure was maintained at P = 12.856 bara for nearly one day. The day after, the pressure had not decreased (it is slightly evolving according to temperature fluctuation of the test room). When hydrogen was released, no cooling was observed on the tank wall, and the quantity of hydrogen vented is small, corresponding to hydrogen contained as a gas phase in the tubes of the circuit and dead (gas) volume of the tank.

The reason why the tank did not absorb hydrogen is probably due to a pollution that came on the surface of the hydride powder in the tank.

Several reasons for the failure of the absorption in the AB hydride tank have been listed and explored:

1) Improper purifying of the test bench gas lines.
2) Improper purity of the hydrogen feeding the test bench
3) A leak of the connections or the tank tightness.
4) A leak of the closing valve of the tank.

After exploring all these reasons, no reason has been found and given. It is a possibility that the standard quality of hydrogen gas is not sufficient, and that the tank would require a very pure feeding hydrogen gas, but the standard test bench made to test conventional hydride tanks (a large number of hydride tank prototypes have already been successfully tested on this bench) have always been fed with this kind of standard hydrogen.

5 Recommendations regarding test benches for flow measurement (mass and volume) of hydrogen in metal hydride tanks

According to the work carried out in the project, some points need to be improved on the construction of an efficient test bench, particularly around the apparatus that was chosen for the measure: the thermal mass flow meter.

Two points have been enlightened as creating measure errors:

1) When using needle valves (static valves) for regulating the mass flows, the mass flow varies drastically during the load or unloading phase, passing from very high mass flow rate to very low mass flow rate, in a short time. This leads to the obligation of having a mass flowmeter dimension on the highest flow rate expected, but then, the low measurable flow rate is too high. It may force the use of several mass flow meter to ensure a higher mass flow rate measure range.

   ⇨ This can be improved using combination of pressure regulators and needle valves.

2) Using a mass flow regulator avoids using several mass flow meters. A mean mass flow is adjusted by the regulation valve, so that a long period of the filling of the tank can be done within the range of the mass flowmeter installed. But, we have discovered that the mass flow measure can have deviation especially if the pressure is low (for a mass flow meter calibrated at a medium pressure between the loading pressure and the unloading pressure).

   ⇨ In order to avoid this, the idea is to work as long as possible near the calibration pressure for the mass flow meter and avoid low pressures.

The main objective is to run the mass flow meter in stable conditions (constant mass flow rate and constant pressure), and if possible, at the same pressure for the loading and unloading phases.

The two best solutions are exposed hereafter. One is guided by the fact that the mass flow meter is not equipped with a flow controller. The other is related to mass flow controller.

5.1 Measurement set-up with mass flow meter and needle valves

5.1.1 Process

The test bench circuit proposed is presented on **Figure 65** for loading situation and **Figure 66** for unloading situation.

To obtain a regulated mass flow, the principle with needle valves is to ensure a quite constant pressure drop on needle valves, that is, to control the pressures before and after the needle valve.

Load

During loading the pressure applied to the mass flowmeter is quite constant and equal to the pressure imposed by BPR_2. Then for the purpose of having a quite constant pressure drop on the needle valve NV_abs, an Upward Pressure Regulator (UPR_1) is used. Thereby, the pressure variation that builds up in the tank is not influencing the mass flow rate during loading too much (in reality, if single stage UPR and BPR are used, regulated pressures vary a bit, but it should be acceptable).

Unload

During unloading the outlet pressure can be considered as stable, particularly if it is atmospheric pressure. So, to ensure a constant pressure loss over the needle valve NV_des, a Backward Pressure Regulator (BPR_1) has been installed before the needle valve.

In that condition the mass flow meter works near the constant outlet pressure (i.e. atmospheric pressure in our case).

5.1.2 Corrections

Due to the intrinsic construction of the gas test circuit, some corrections have to be brought to the quantity of gas introduced in the tank branch. All this is due to the analysis of knowing what quantity of hydrogen has passed through the mass flowmeter, and what quantity did not pass through it, but is nevertheless admitted in the tank circuit.

We do not describe here the calculations to be done when really wanting to know the quantity of hydrogen that has is really contained in the tank, or even better, in the hydride. For this we are supposed to know the gas volume of the tube of the circuit, and the dead volume in the tank, namely Vol3 on **Figure 67**.

The correction addressed hereafter concerns the two volumes Vol1 and Vol2 described in **Figure 67**. These volumes are more or less critical when passing from different states of the test bench. The important thing is to know the quantity of hydrogen that has passed to Vol3. These transition situations are described in **Figure 68**.

Transition LR: when passing from absorption (loading) to repose phase, the quantity[1] $(P_{source} - P_{tank})Vol2$ have to be added to the mass of hydrogen that has entered in the tank circuit. Note that this quantity is quite small if loading is stopped at the end of the loading because at this moment, P_{source} and P_{tank} are quite close.

Transition RU: When passing from repose state to unloading state, the quantity of hydrogen contained in the Vol1 volume will be evacuated without passing through the mass flowmeter. This has to be taken into account. The quantity $\left(P_{repose} - P_{atm}\right) Vol1$ have to be remove from the quantity of gas present in the tank circuit.

Transition UR: When passing from unloading state to repose state, some part of the gas that has escape the tank circuit volume is still contained in the volume Vol2 before the mass flow. This quantity is: $P_{outlet}Vol2$. It is usually quite small.

Transition RL: And finally, when passing from repose state to loading state, one has to add the quantity $P_{equilibium}Vol1$ that is already situated after the mass flow and is now part of the hydrogen admitted in connection with Vol3.

Please note that other solutions exist to pilot V_V1, V_V1b, V_V2 and V_V2b. For instance, by unlinking the aperture of V_Vxb to the opening of V_Vx and doing this sequentially (this solution obliges to have two more control channels for piloting independently V_Vxb valves).

But still, the corrections by the volume Vol1 and Vol2 have to be done as well (considering different pressure states).

Another important problem concerns the volume entrapped before the flowmeter find itself in the situation where the upward pressure is relatively high pressure compared to the downward pressure. The volume of gas will then pass very quickly through the mass flowmeter, saturating its measure range. We can call this the "saturation" effect. During this phase, the measure may be quite imprecise. Let examine for which transition phase this can happen.

Transition RL: during this phase, a sudden high pressure will be brought to the upward part of the mass flowmeter. The mass flowmeter will be saturated. There are chances that it is saturated until the back volume has reached its equilibrium pressure imposed by UPR_1.

Transition LR and UR: during these phases, as V_V1b and V_V2b open at the same time, the pressure on both sides of the flowmeter equilibrates. There is no "saturation" effect in those cases.

Transition RU: during this phase, Vol1 is evacuated very quickly, so the mass flowmeter has potentially a high upward pressure. This will saturate the mass flowmeter probably until the pressure in the volume Vol2+Vol3b has decreased.

This kind of deviation in the measure (period of saturation of mass flowmeter) is difficult to correct. The main conclusion is to reduce to the minimum Vol1 Vol2, Vol3a and Vol3b.

Remarks

Note that with a mass flow controller (not only a mass flowmeter), this problem can be handled by starting the measurement with a closed controller valve and open it slowly to avoid the "saturation" effect. This is possible as long as the mass flow controller can be efficiently piloted although submitted to a high pressure difference.

[1] We consider here that the gas obeys a perfect gas law. If not, other more complex formulas must be used.

Another final remark: This study has been conducted supposing that the operation on the valves are perfectly synchronized, for instance, that when V_V2 is closed, V_V2b opens exactly at the same time. In real life, this does not happen this way, one valve may open or close before the other. This can lead to deviation on the real quantity of hydrogen measured. A study should be conducted on this point, and recommendation may be issued on preferable prioritization on the order of valve opening and closing, e.g. by temporization.

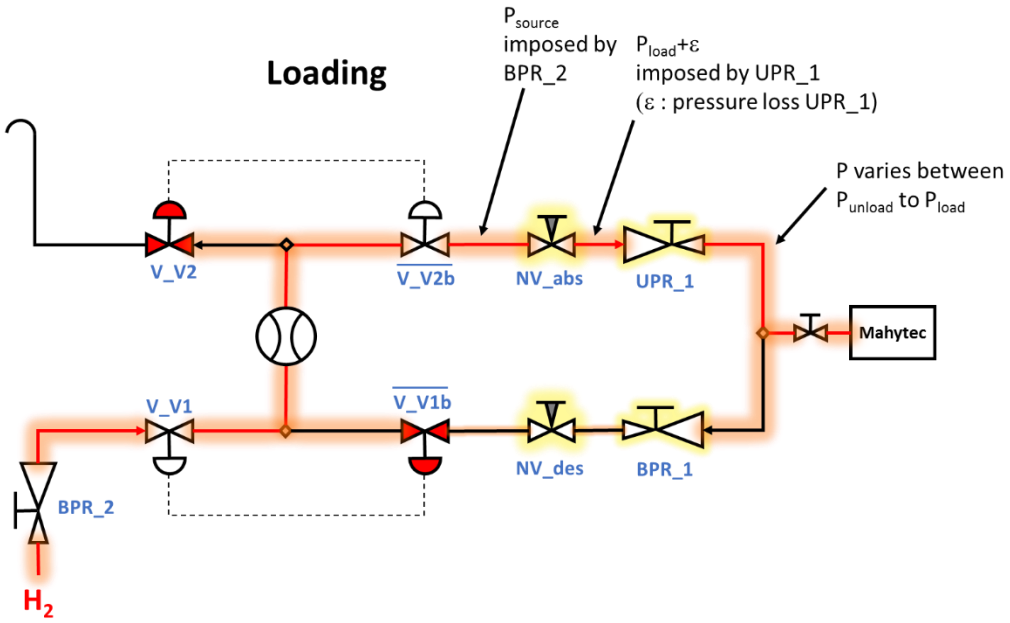

Figure 65 – Gas circuit of test bench with needle valves during loading.

BPR: Backward Pressure Regulator, UPR: Upward Pressure Regulator, V_Vx: Valve, NV: Needle Valve

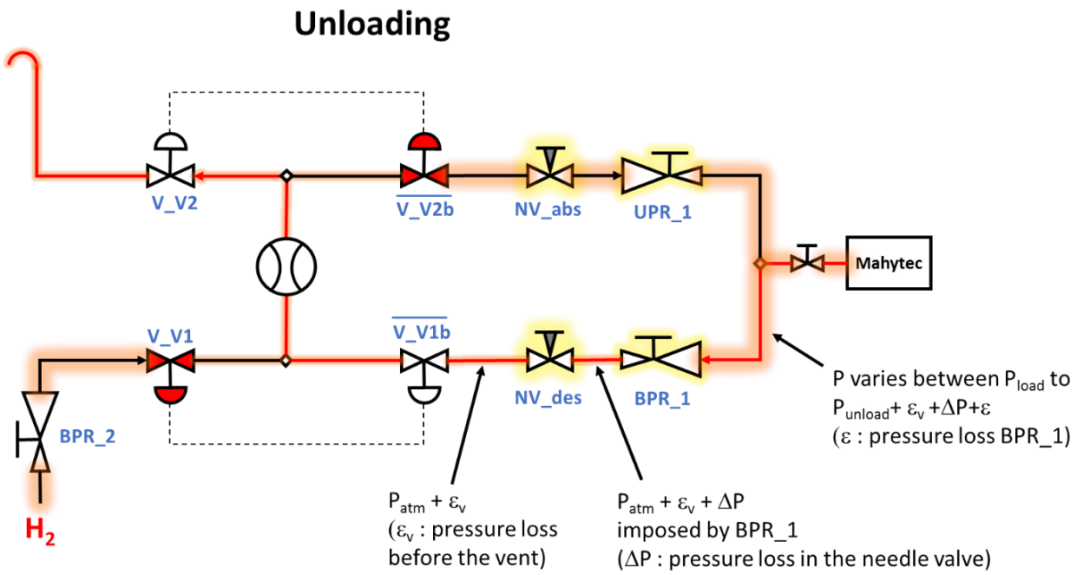

Figure 66 – Gas circuit of test bench with needle valves during unloading.

BPR: Backward Pressure Regulator, UPR: Upward Pressure Regulator, V_Vx: Valve, NV: Needle Valve

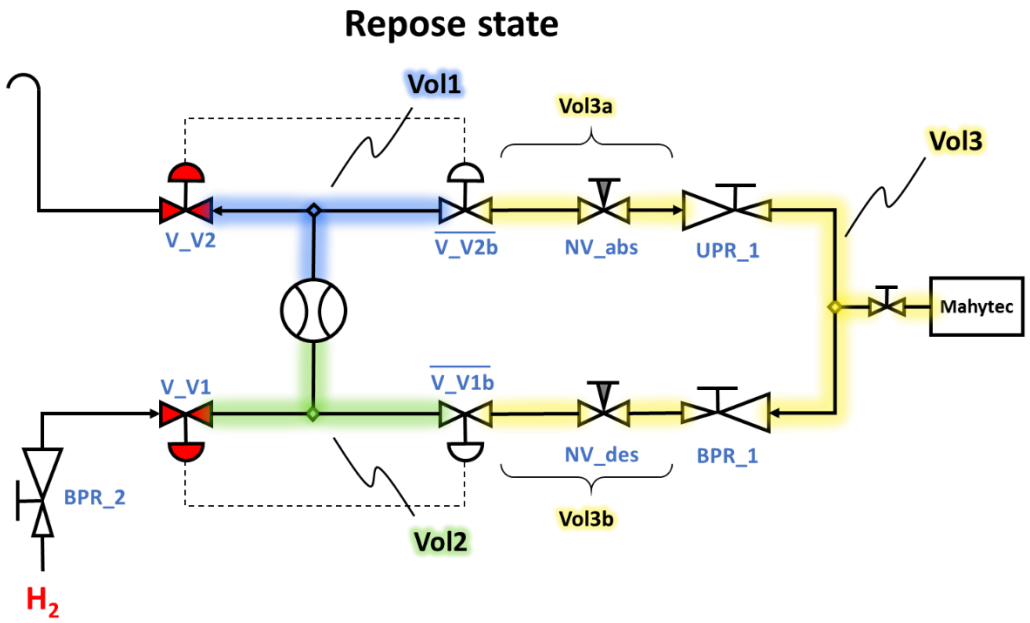

Figure 67 – Volumes of interest for correction of transition between loading, repose and unloading phases of the tank testing.

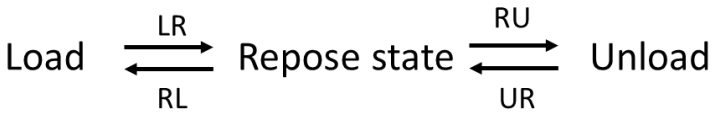

Figure 68 – Different transition phases between operations of the test bench.

5.2 Measurement set-up with mass flow controller

5.2.1 Process

The test bench circuit proposed is presented on **Figure 69** for loading situation and **Figure 70** for unloading situation.

In this situation, with the use of a mass flow controller, the gas circuit is a bit simpler than with needle valves.

For the loading, V_V1 is opened, so the pressure source imposed by BPR_2 is applied on the mass flow controller, which will regulate around a desired mass flow rate. The pressure after the mass flow controller will vary from the initial pressure (let say it is approximately P_{unload} if the state before was a fully discharged state) to the maximum pressure near the source pressure.

For the unloading, as the pressure in the tank will decrease from P_{load} to P_{unload}, and in order to avoid that the mass flow controller is submitted to a varying pressure, we have inserted a pressure reducer BPR_1 so that the pressure that is applied to the mass flow controller and mass flowmeter is the same. It is adjusted around the outlet pressure that means near the atmospheric pressure.

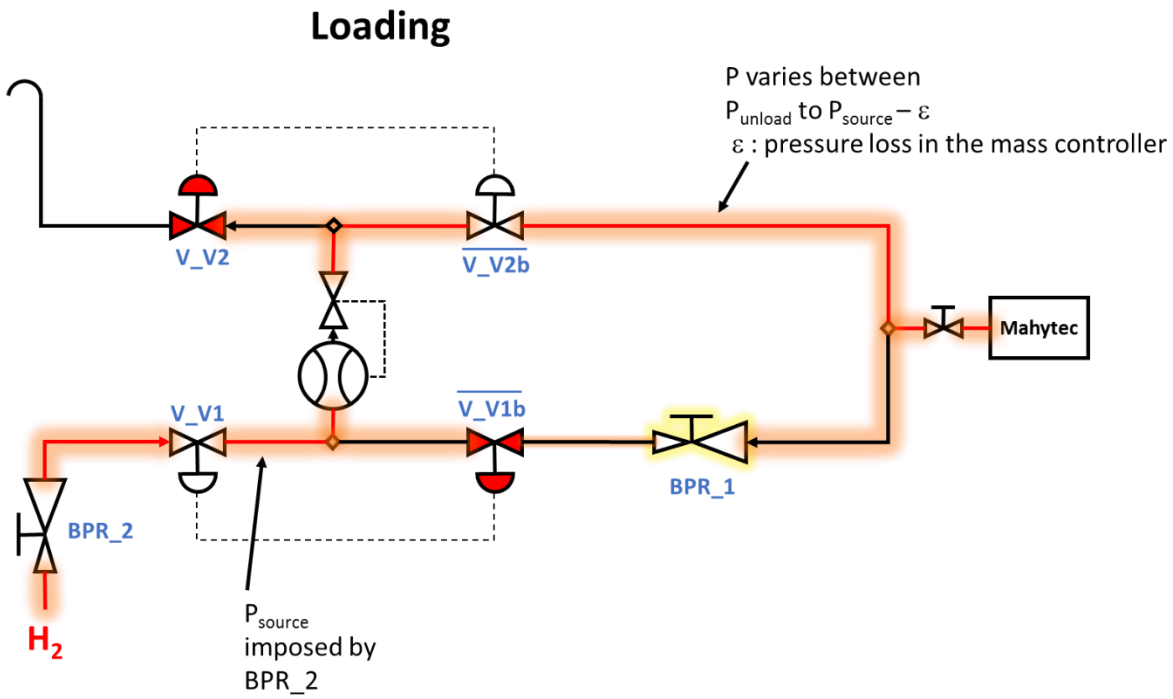

Figure 69 – Gas circuit of test bench with a mass flow controller during loading.

BPR: backward pressure regulator, V_Vx: Valve

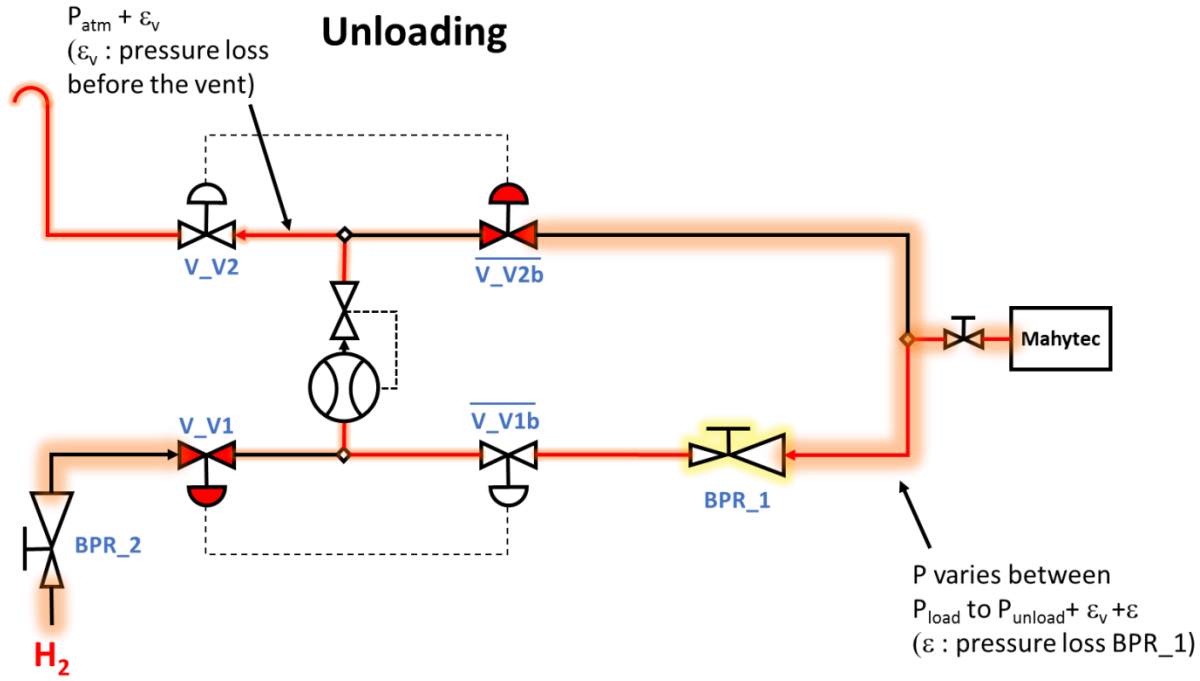

Figure 70 – Gas circuit of test bench with a mass flow controller during unloading.

BPR: backward pressure regulator, V_Vx: Valve

5.2.2 Corrections

With this gas circuit arrangement, the same kind of correction described in **section 5.1.2** has to be made concerning Vol1 and Vol2. Nevertheless, there is no need to worry about the "saturation" effect, unless the regulation valve does not behave conveniently (we have observed seldom small "saturations" during our experiments because the valve was jamming a bit: even though we ordered a small aperture to begin the load or unloading phase, it open a bit too much for a very short time, the PID controller had some difficulties to pilot the valve aperture. This is likely to occur when pressure difference applied on the valve is high. We may consider that the quantity of hydrogen which have saturated the mass flowmeter is negligible, but the best is to work with high quality and well adapted mass flow controller which permits to avoid this phenomena).

5.3 Conclusion concerning both approaches

Design with needle valves

Concerning the design with needle valves, this construction of the test bench allows for constant flow rates during loading and unloading, but the mass flow meter works at two different pressures: during loading, it is fixed by BPR_2, during unloading it is fixed by the outlet pressure (atmospheric pressure in our case).

Adding those needle valves, UPR and UPS restrain the pressure range attainable because of the pressure loss they introduce in the circuit. The most visible consequence will be that mass flow rate for the end of each loading or unloading period will be reduced, and some of the capacity measure of the tank will be restrained by earlier cut-off of the mass flowmeter measure.

Design with mass flow controller

Concerning the design with a mass flow controller, this design is a bit simpler than with needle valves. It permits to control the flow rate that does not vary too much during the measure, but the pressure of use of the mass flow meter is not the same when loading and unloading.

Summary

Both solutions require the mass flowmeter to work under different pressure for loading and unloading phases. Around source pressure for the loading, and around the outlet pressure (here it is the atmospheric pressure) for the unloading phase. Thus, both solutions require a calibration of the mass flowmeter at two pressures.

The idea of using needle valves was guided by the choice of avoiding using a mass flow controller, but this solution includes a gas circuit which is a bit more complicated (with more components), and it suffers from a pronounced "saturation" effect, which makes the mass flowmeter to work in a saturated state and is expected to generate an uncontrolled measure deviation.