

Hydrogen

WP3 reporting

Measuring the hydrogen capacity of hydride tanks

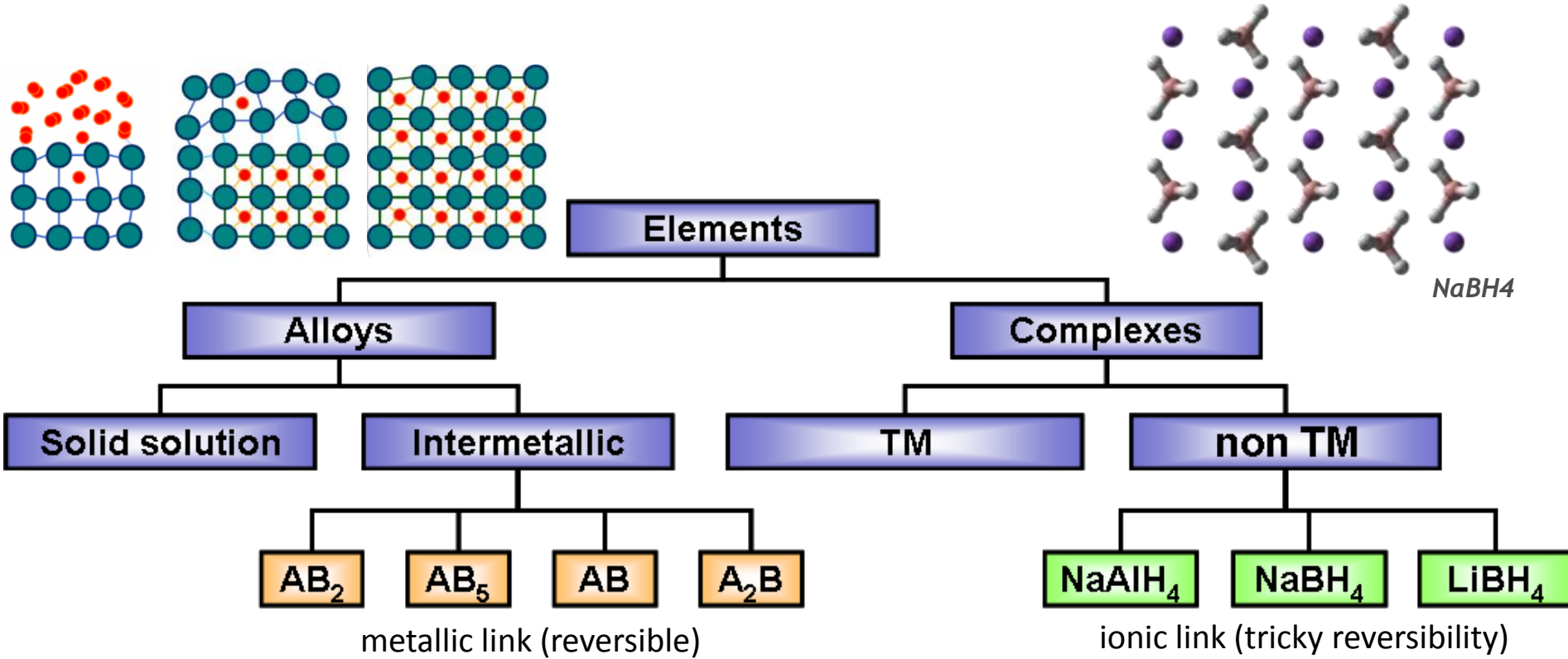
Oliver Büker | Benoit Delobelle | Olivier Gillia | Rodrigo Perez



The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

- ❖ Introduction – Presentation of hydride storage
- ❖ ISO16111
- ❖ Different way to measure the hydrogen capacity of a tank
- ❖ Thermal mass flowmeter : details
- ❖ Tank manufactured and initially tested by Mahytec
- ❖ Test bench and results from FHA
- ❖ Test bench and results from CEA
- ❖ Recommendations for optimized testing devices
- ❖ Conclusions and perspectives

A few words on hydride storage



Intermetallic Hydrides

- ❖ no progress expected in capacity, but work well
- ➔ research of low cost

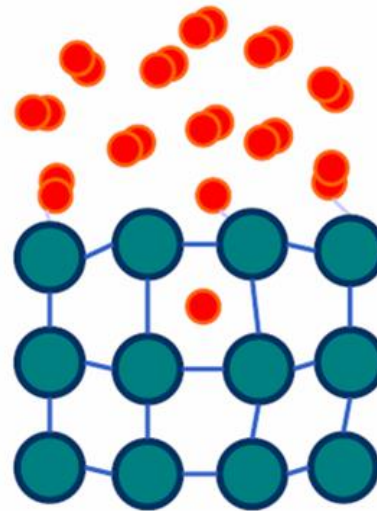
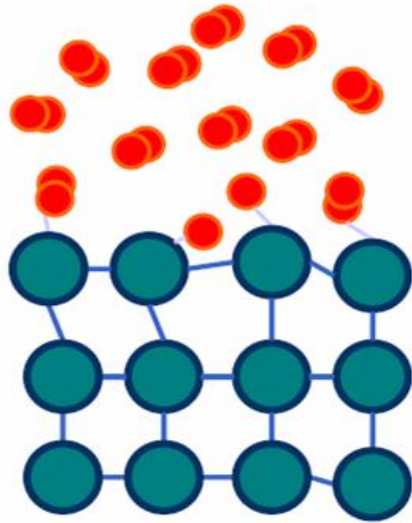
➔ Search for low cost precursor (i) impurities
(ii) fundamental research : influence of impurities on the absorption capacities

Complex Hydrides

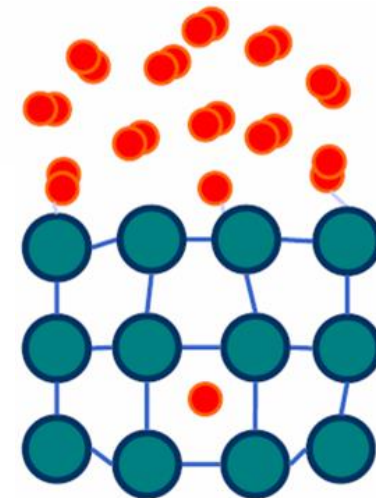
- ❖ potential progress or rupture, but not working well
- ➔ alanates, $\text{LiBH}_4 + \text{MgH}_2$, LiNH_2

➔ Desequilibrate the thermodynamics and obtain reversibility

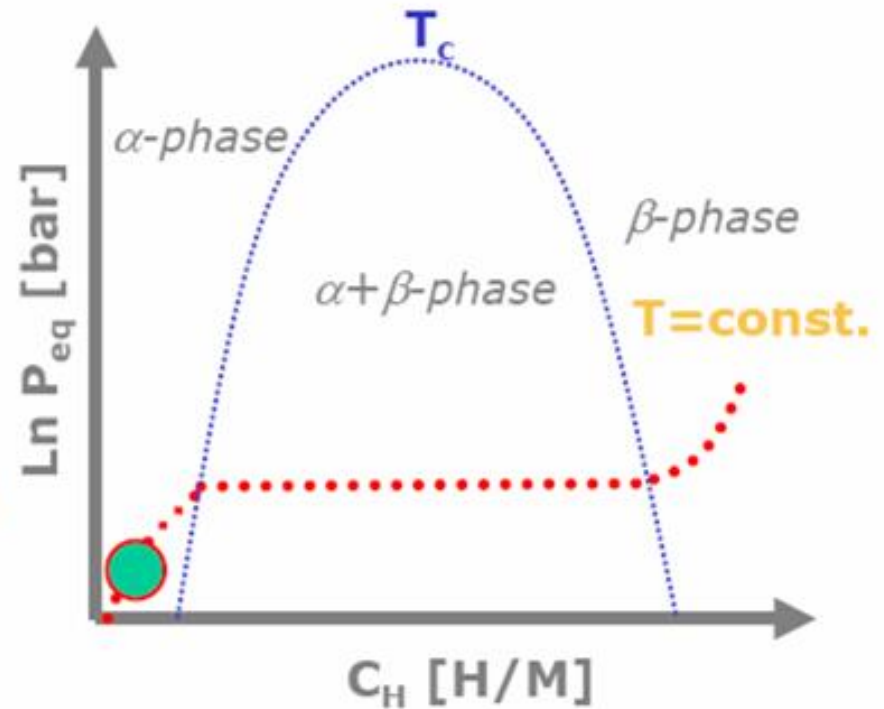
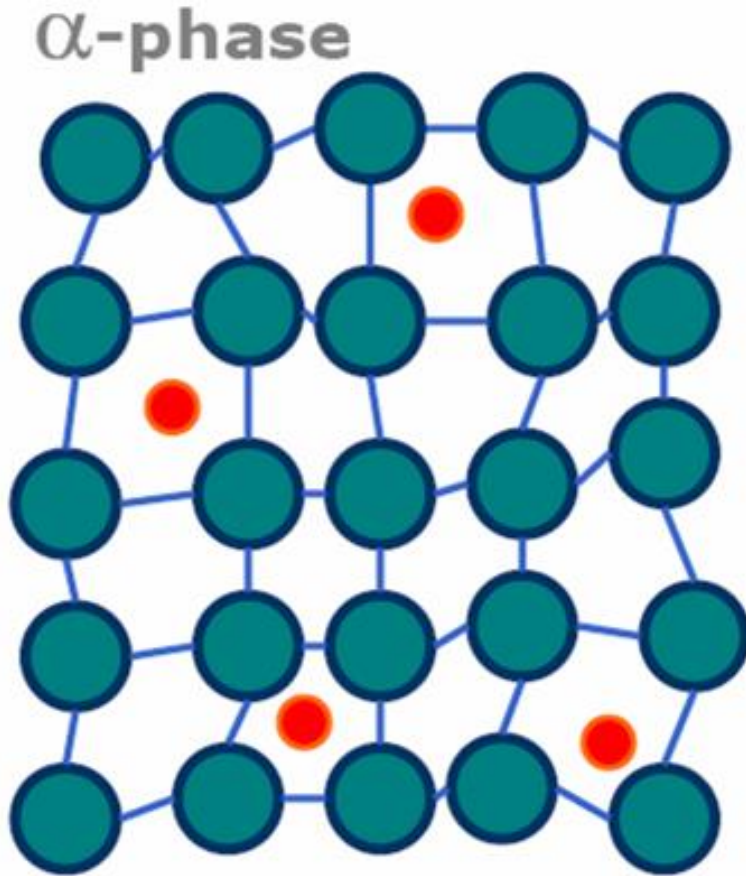
- nanoconfinement
- catalysis
- hybridation of materials ($\text{LiBH}_4 + \text{MgH}_2$)

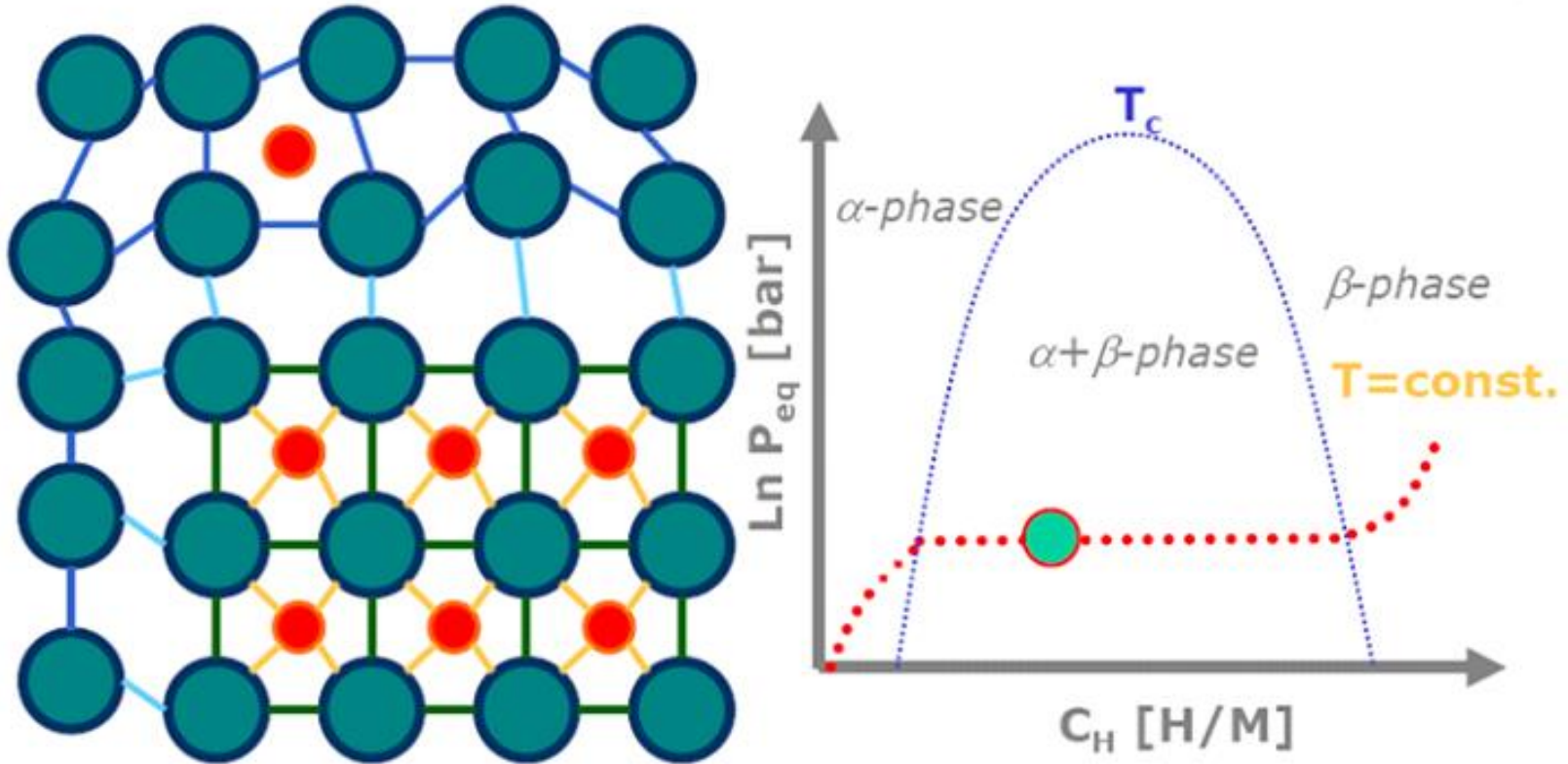


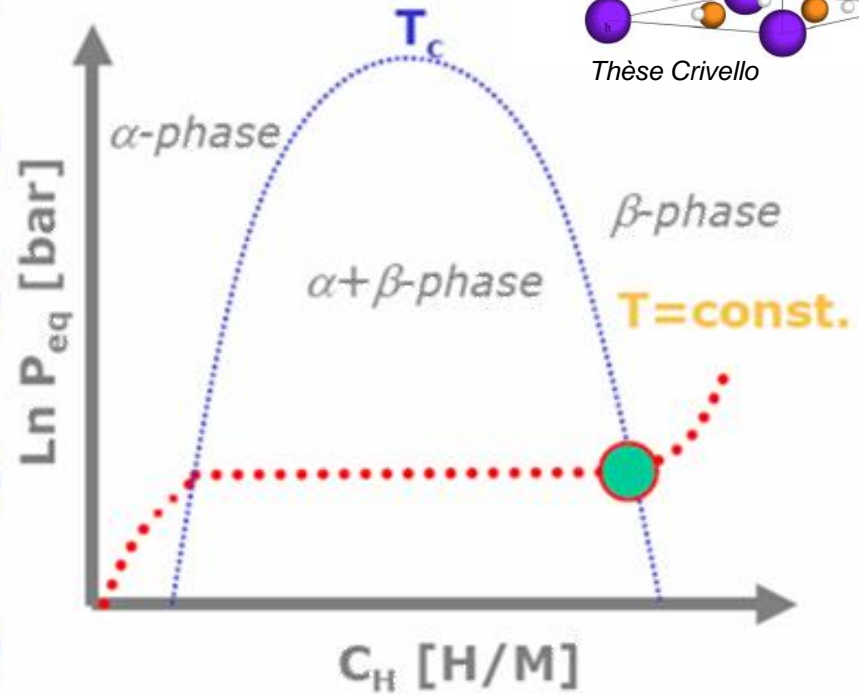
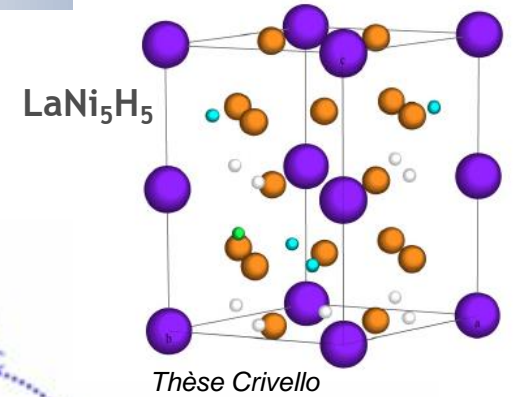
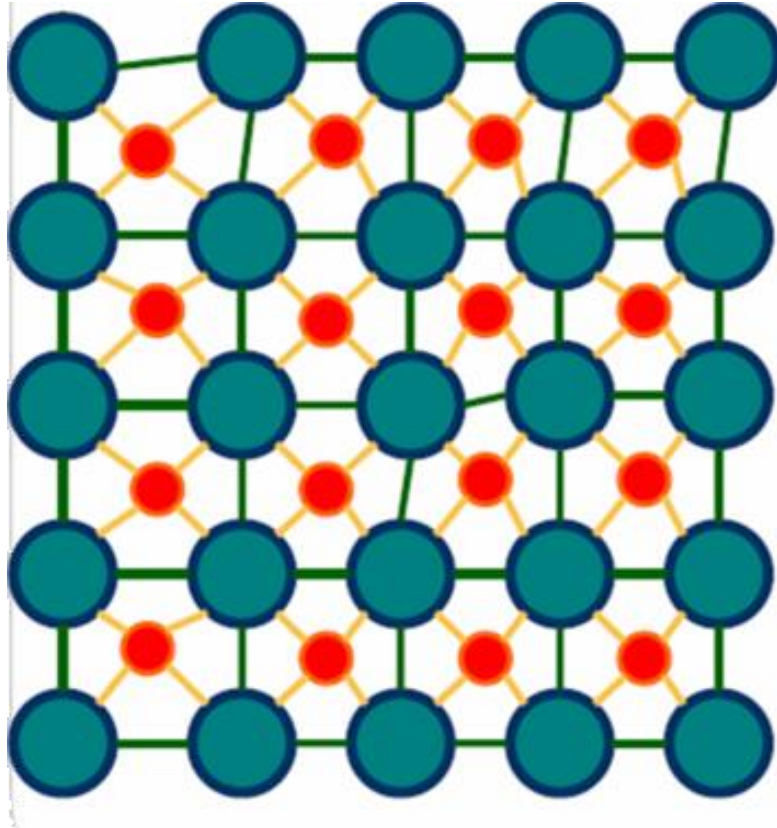
α -phase
(solid solution)



H-diffusion

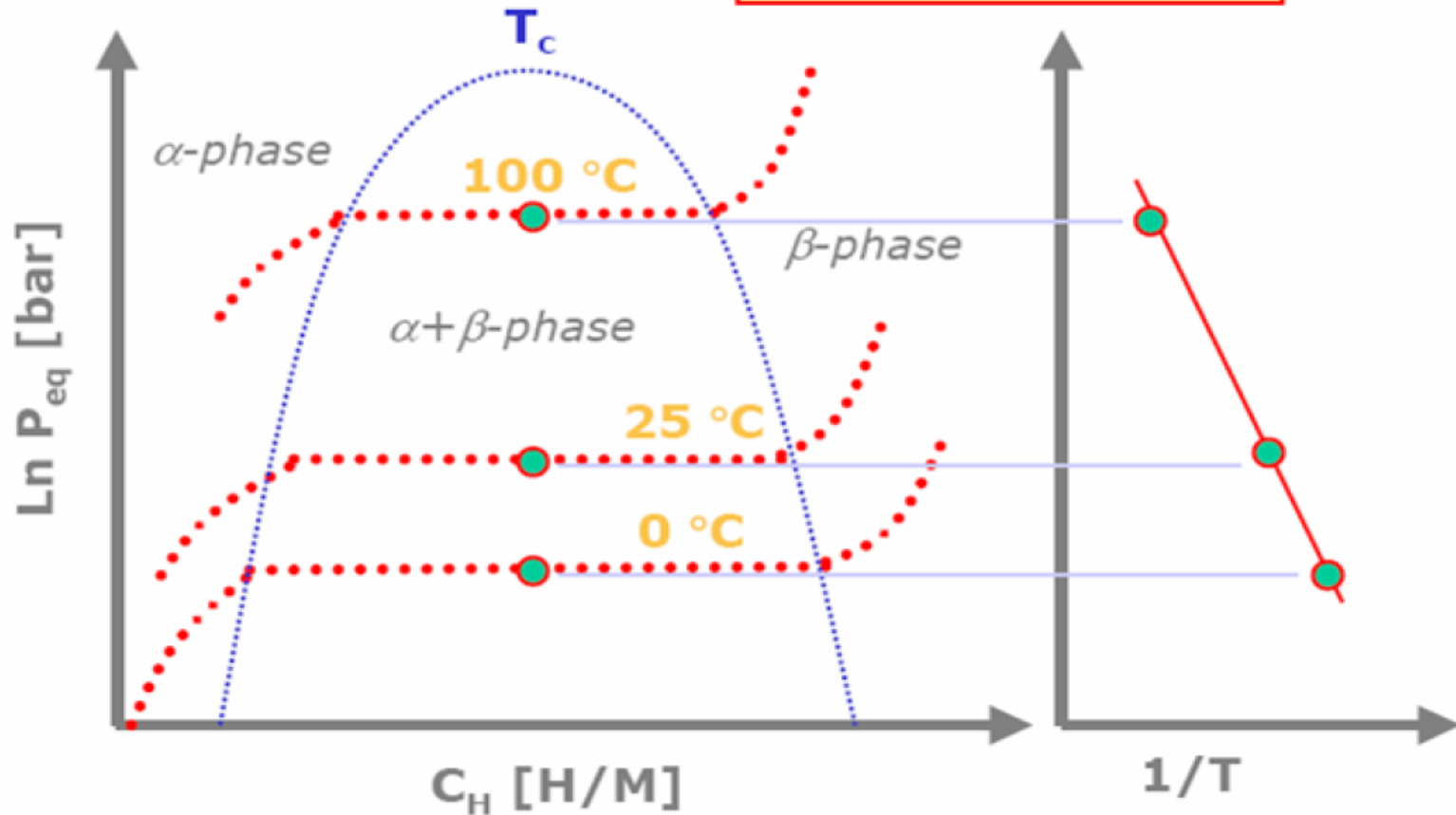




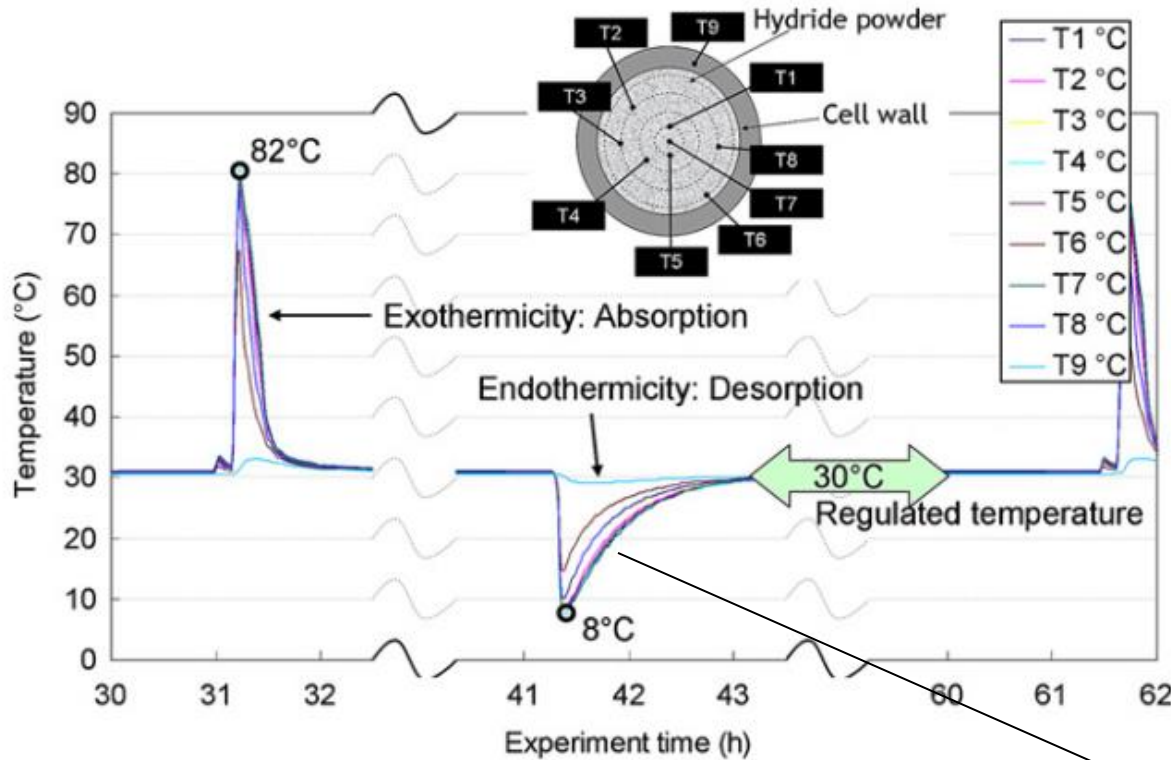


Van't Hoff law

$$\ln P_{eq} = -\frac{\Delta S^0}{R} + \frac{\Delta H^0}{RT}$$



Matériau : TiVCr (BCC) – 0 – 40 bars at 30°C

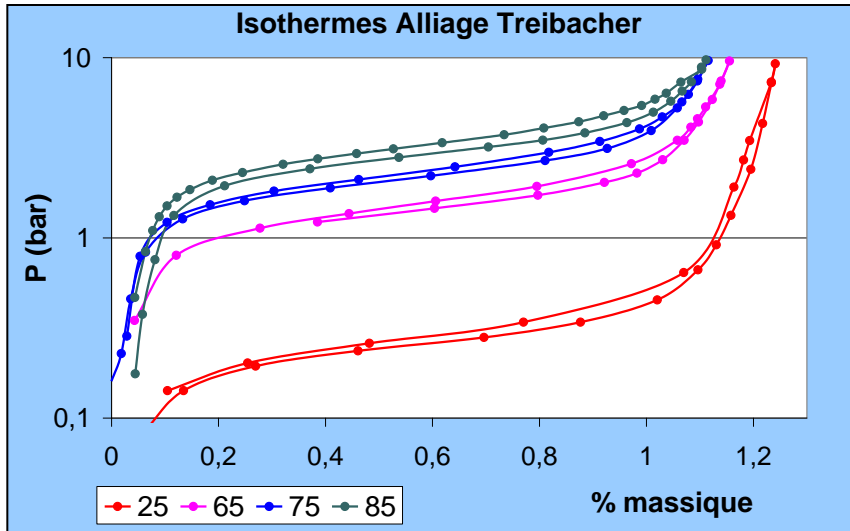
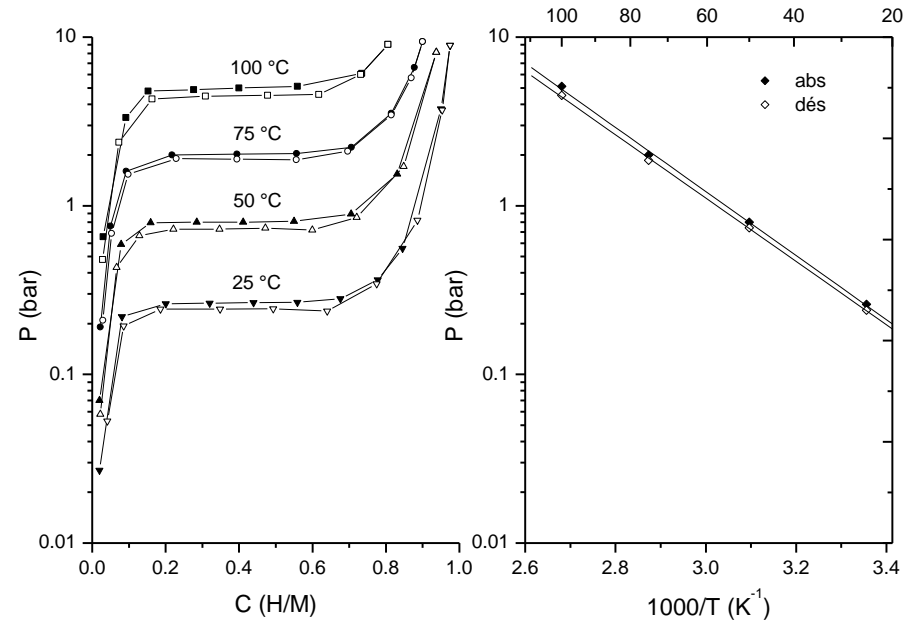
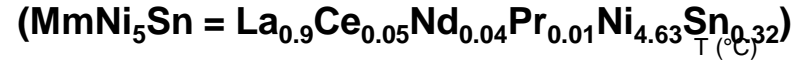
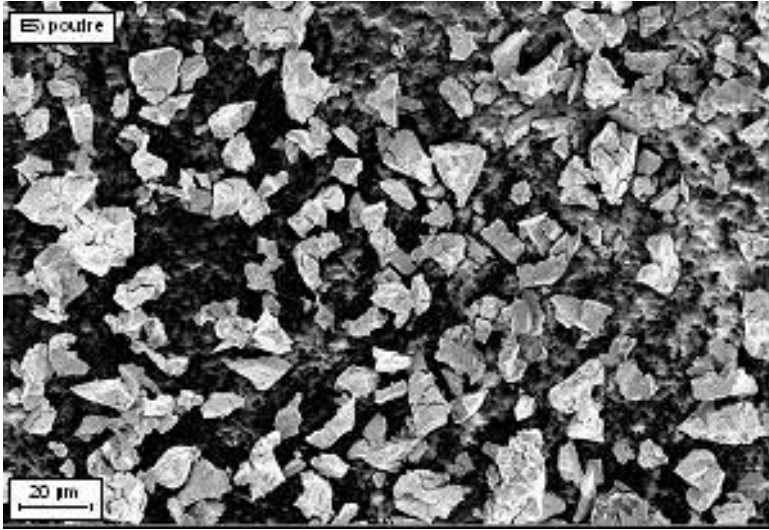


Article : B. Charlas, O. Gillia, P. Doremus, D. Imbault, *Int. J. H. E.*, 2012

→ Cooling due to desorption

→ security if leaks : auto-cooling and stopping

MmNi5 (LaNi5) laboratory alloy

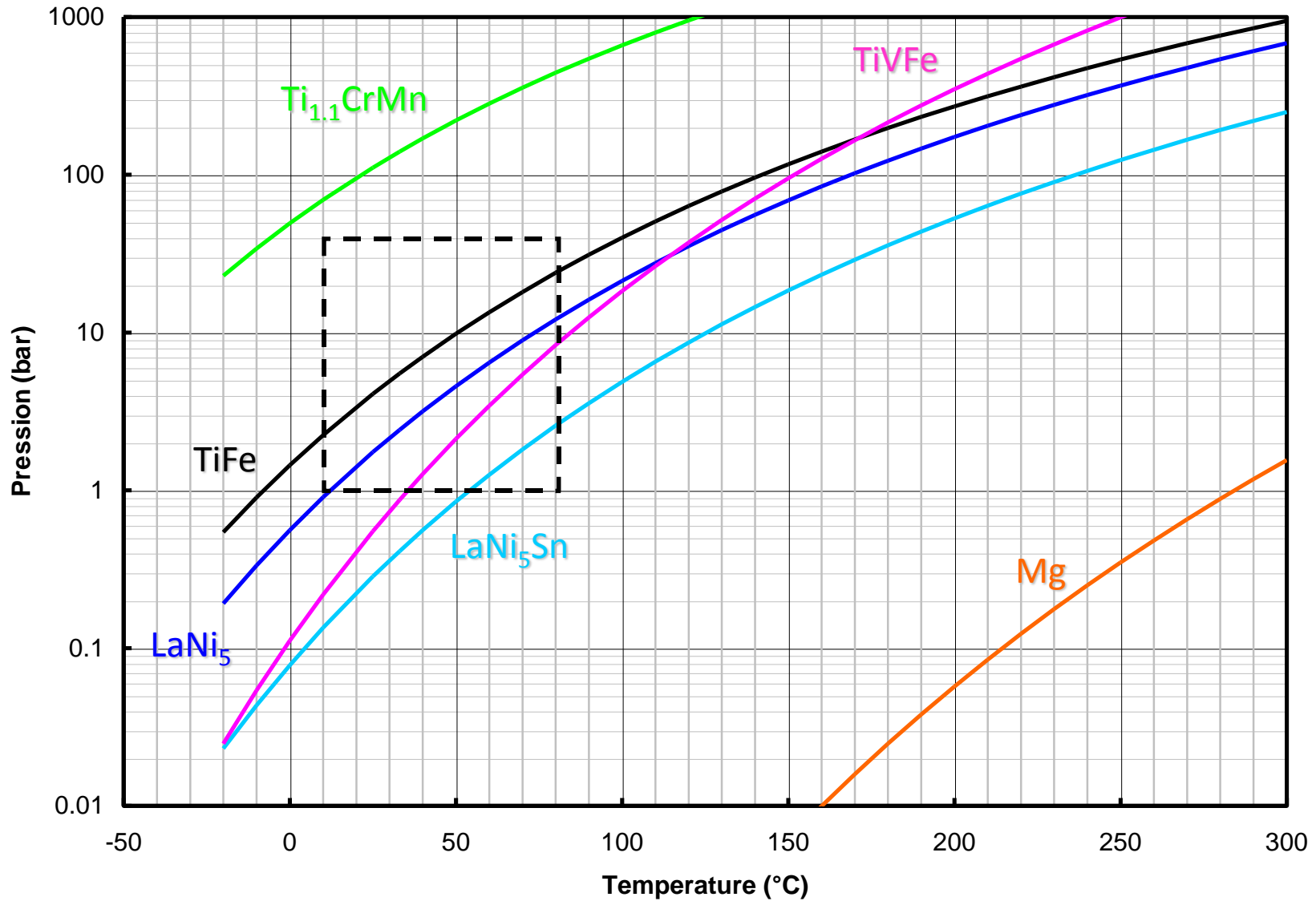


Industrial alloy of the same formulation

M. Botzung Ph.D

Family	Compound	Max weigth capacity (%)	Temp. (°C) at P=1 bar	Kinetics	ΔH (kJ/mol)
AB	FeTi	1.8	-8	Fast	-28.1
AB ₅	LaNi ₅	1.49	12	Very fast	-30.8
AB ₂	Ti _{0.98} Zr _{0.02} V _{0.43} Fe _{0.09} Cr _{0.05} Mn _{1.5}	1.9	-28	Very fast	-27.4
BCC	(V _{0.9} Ti _{0.1}) _{0.95} Fe _{0.05}	3.7	36	Fast	-43.2
A ₂ B	Mg ₂ Ni	3.6	255	Mean	-64.5
complexe	NaAlH ₄	7.5	180	Mean	-70
Single element	Mg	7.6	279	Slow	-74.5

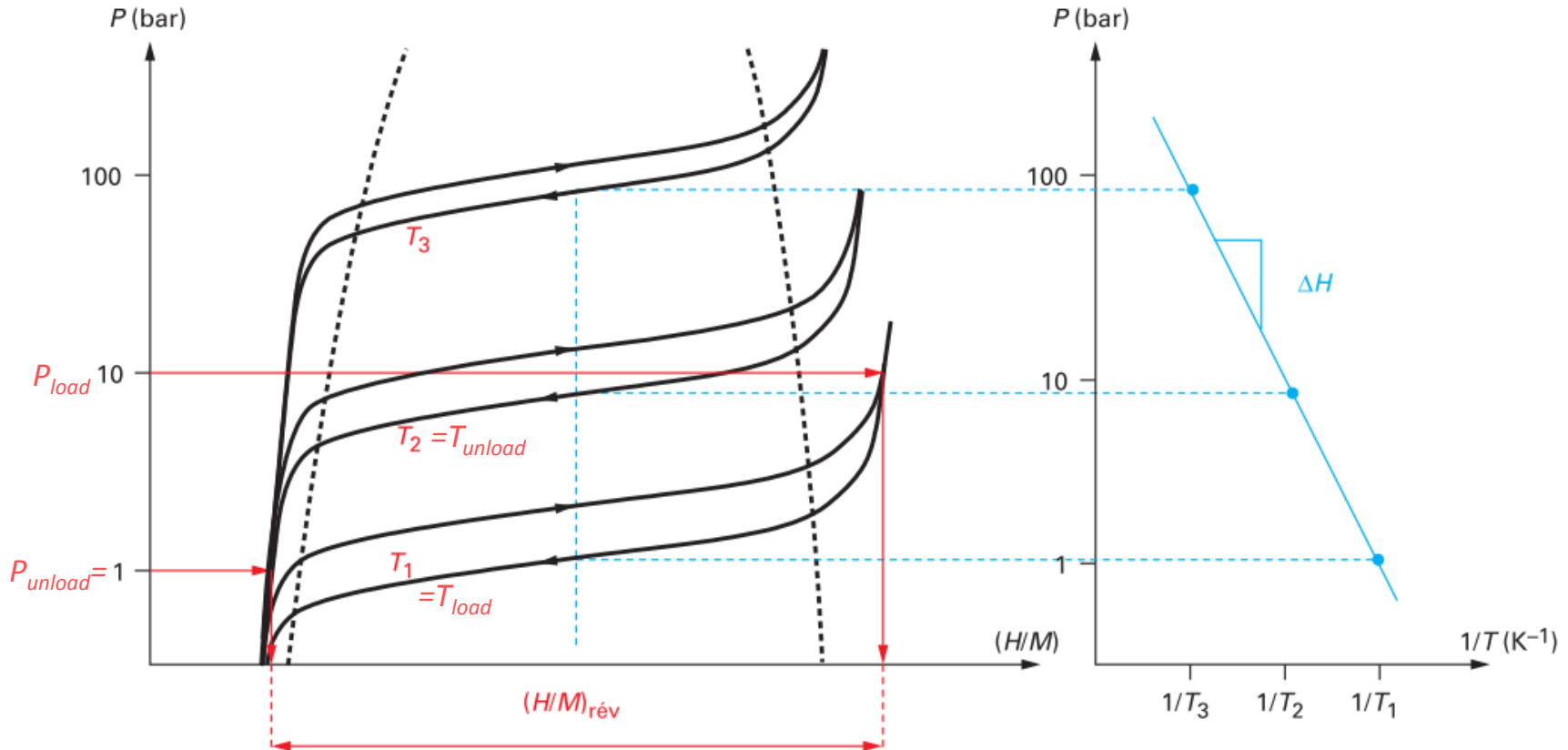
source : Sandrock review paper, 2003



The hydride reversible capacity is linked to **operating conditions**

operating temperature range [T_{load} : T_{unload}]
operating pressure range [P_{load} : P_{unload}]

! in ISO16111, the operating temperature range differs from service temperature range which is at least [-40:65] °C



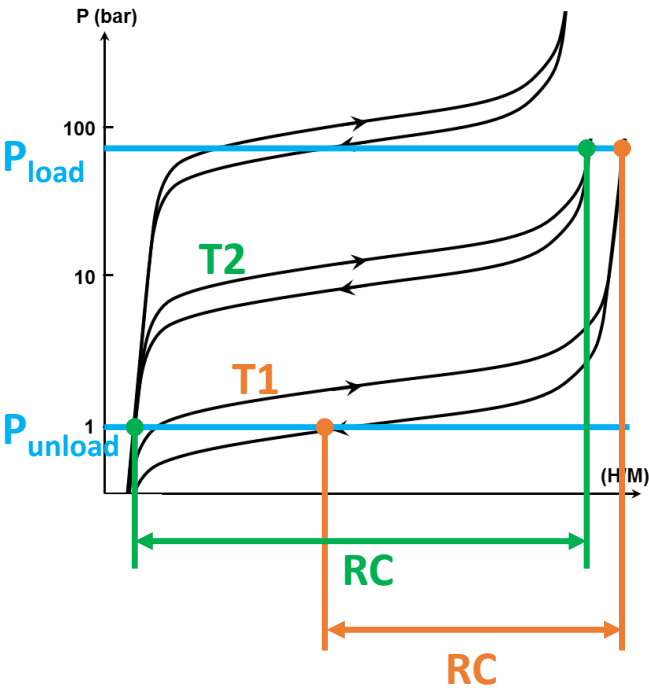
Hydride reversible capacity

e.g. RC : rated capacity on ISO16111

Pressure piloting

$T = \text{cst} = T1 \text{ or } T2$

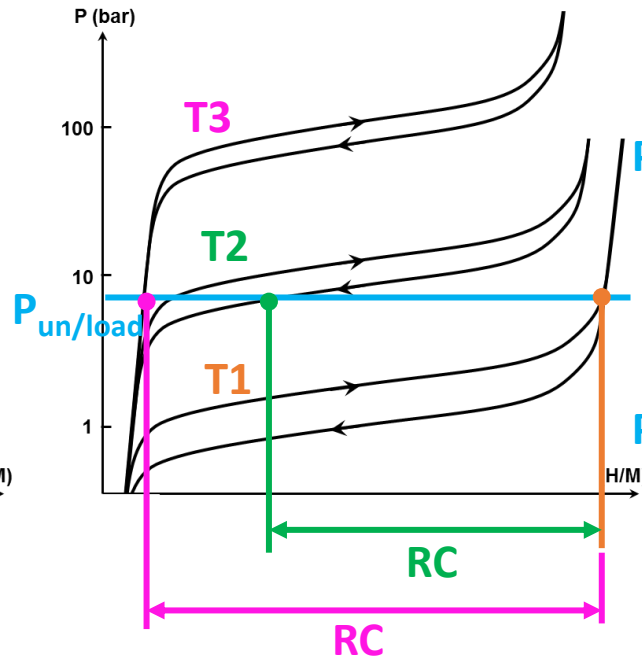
$P = P_{\text{unload}} \text{ to } P_{\text{load}}$



Temperature piloting

$T = T1 \text{ to } T3$

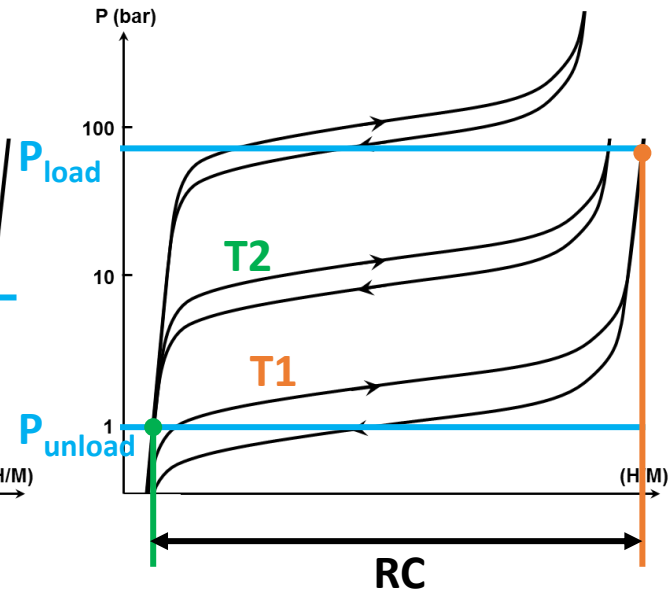
$P = P_{\text{un/load}}$



Both

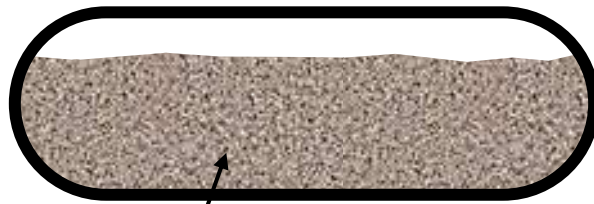
$T = T1 \text{ to } T2$

$P = P_{\text{unload}} \text{ to } P_{\text{load}}$



Tank reversible capacity > Material reversible capacity

Tank reversible capacity shall include the hydrogen in the hydride as well as the hydrogen in gaseous form



$$V_{gas} = V_{sky} + V_{porosity}$$

$$n_{tot} = n_{hyd} + n_{gas}$$

$$\downarrow$$
$$RC$$

$$\downarrow$$
$$n_{gas}$$

$$= \frac{P_{load} V_{gas}}{Z(T)RT}$$

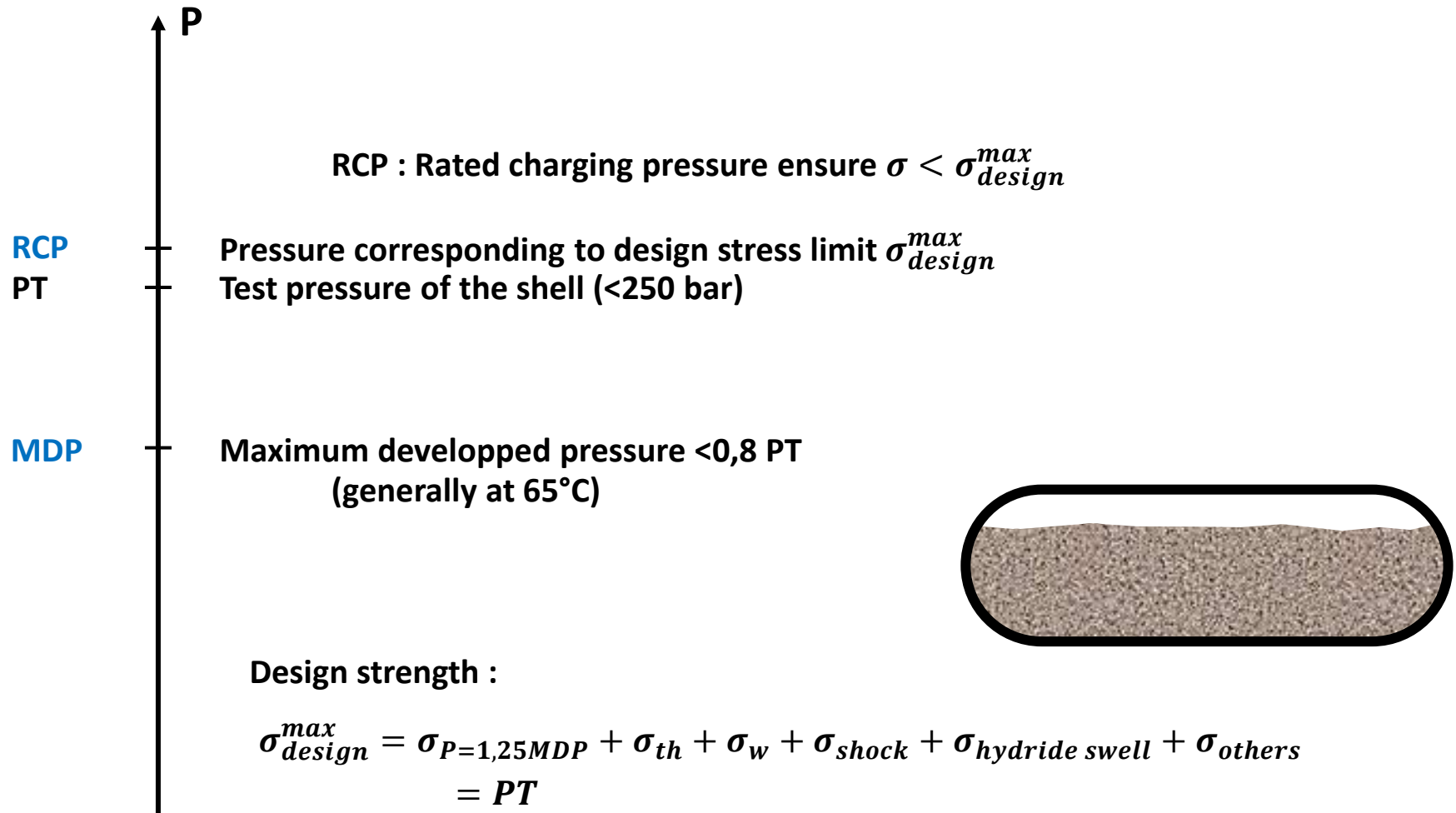
INTERNATIONAL STANDARD

ISO 16111

First edition
2008-11-15

Transportable gas storage devices — Hydrogen absorbed in reversible metal hydride

*Appareils de stockage de gaz transportables — Hydrogène absorbé
dans un hydrure métallique réversible*



Fire test

- 1 MH tank

Burst test

- 3 MH tank

Drop test

- 1 MH tank

Leak test

- 1 MH tank

Hydrogen cycling

- 5 to 6 MH tank

Shut-off valve impact test

- 3 MH tank

Thermal cycling test

- 5 to 6 MH tank

Batch test

- Pressurize to destruction

+

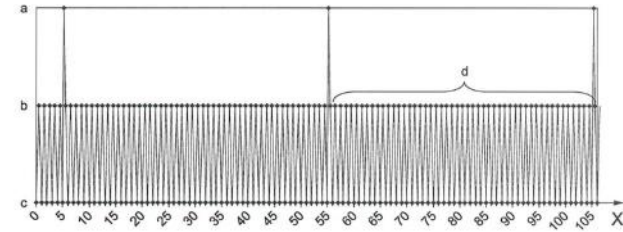
Cycle test

for those used in a single orientation : **5 tanks** in that orientation

for those used in a single orientation : **2x3 tanks** in perpendicular orientation, horizontal and vertical

cycle between <5% of RC and >95% of RC

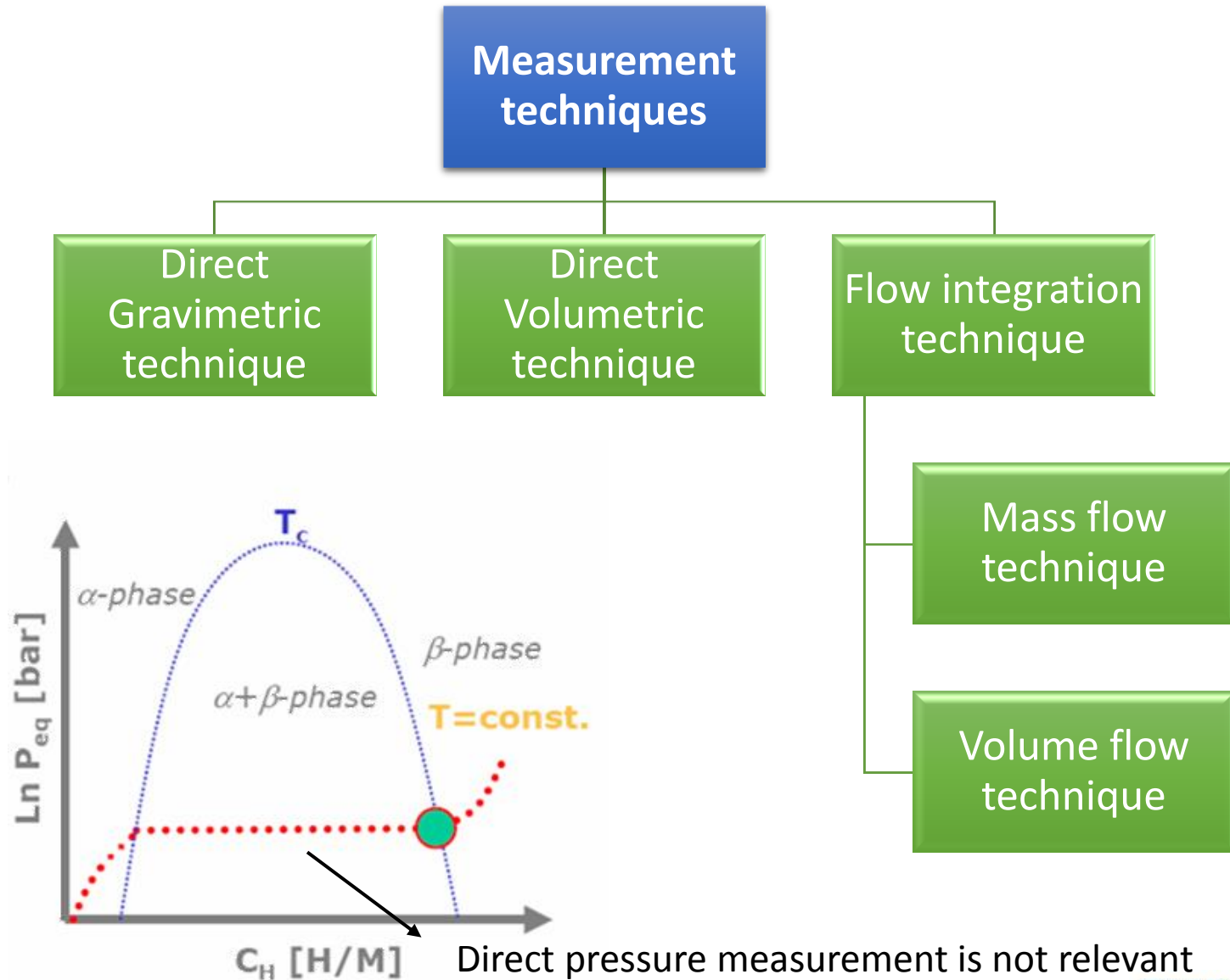
at pressure $P=RCP$ for loading (and for unloading ?)



minimum number of cycles

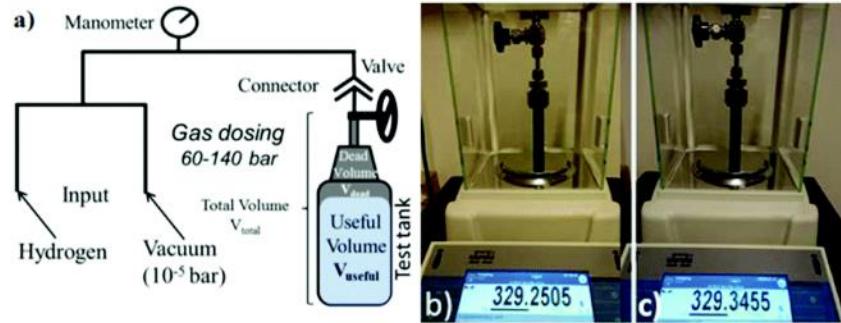
repeat until if strain measured at loaded state :

- for gages with strain $> 0,5$ strain design limit is stable → **success**
- is exeeding the strain design limit or plastification is observed → **failure**



Direct pressure measurement is not relevant

The idea is simply to weigh the absorbed gas (hydrogen)



Need very precise scale as H₂ is light :
AB tank : 0,8 kg H₂ / 100 kg system

A lot of uncertainties coming from :

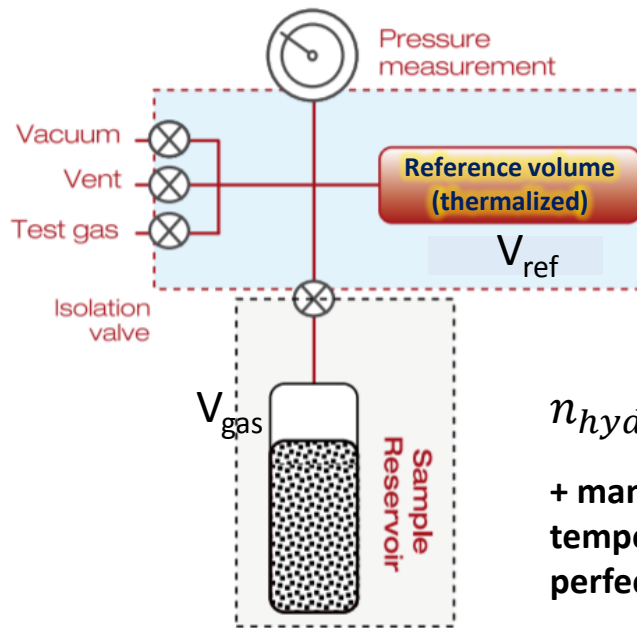
- weigh and stiffness of connection
- air movement around the tank



SCALES

Sievert method, based on 2 points:

- Calibrated volumes
- Pressure measurement



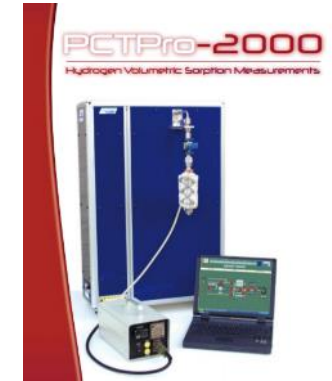
$$n_{hyd} \propto (P_{initial} - P_{final})V_{ref}$$

+ many corrections on V_{gas} ,
temperature, sub-volumes, non
perfect hydrogen gas

- Be careful of (long) transient thermal effects

➔ more often used as incremental to precisely determine the PCT curve

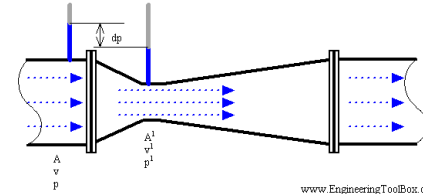
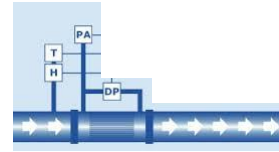
Commercial PCT products
examples:



Flow integration method

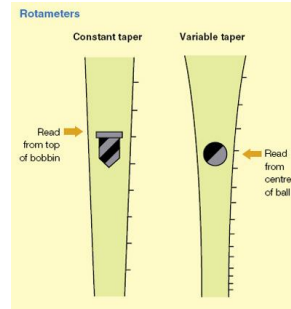
Volume flow techniques
Others

Pressure drop

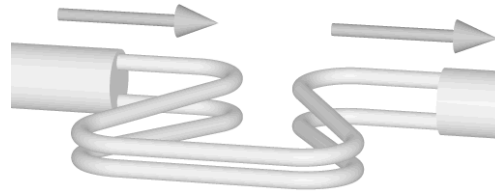


www.EngineeringToolBox.com

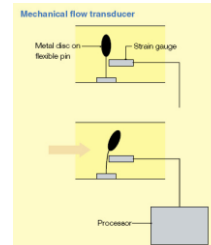
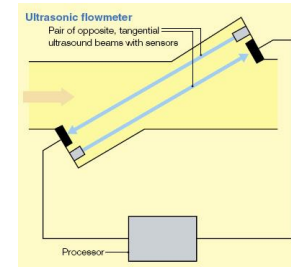
Rotameter



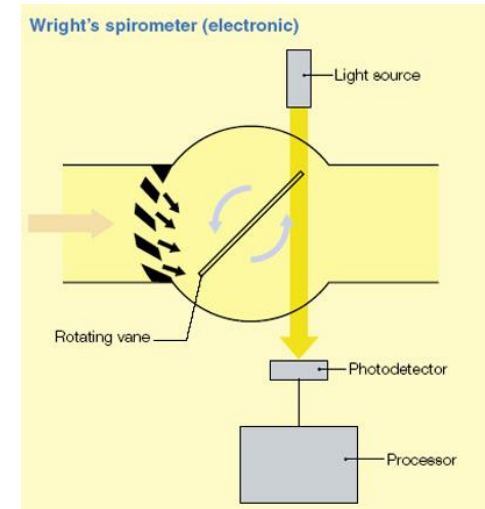
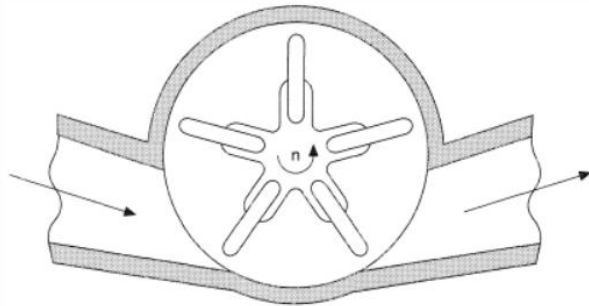
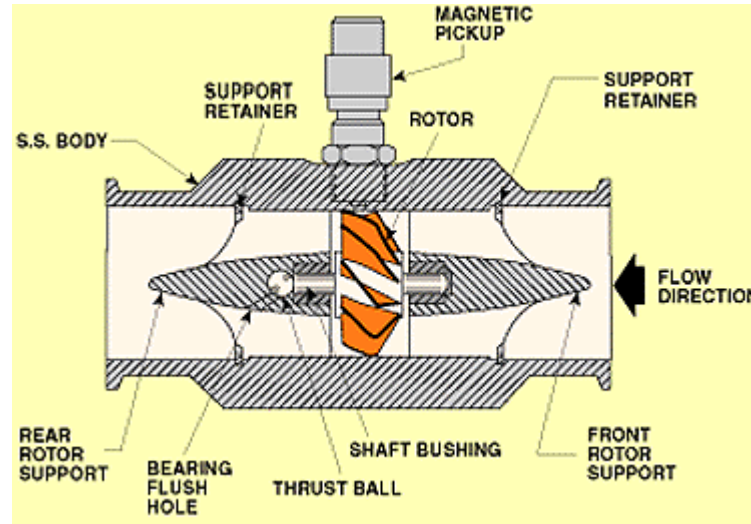
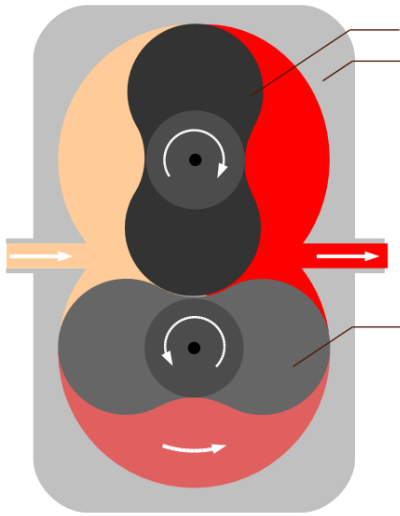
Coriolis



Others
(US, deflection,...)

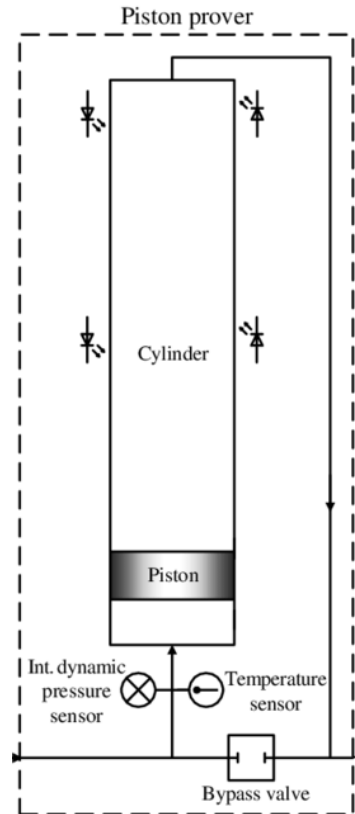


Volume count flowmeter : 1 rotating

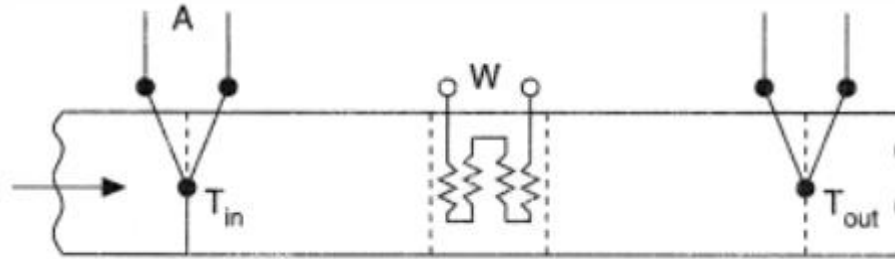


Rotation speed is related to volume flow :

- not very precise (leaks, flow regime sensitivity)



Volume discrete counting ($V/\delta t$ is the volume flow)
Quite precise, used as calibration device



- Easy to use
- Composition of gas has to be known
- No traceability compared to other techniques (e.g. critical nozzles)

Need to be calibrated in order to provide traceability to SI units

No Europe NMI's provide direct traceability to H₂

→ need a conversion factor

→ very often calibrated with He

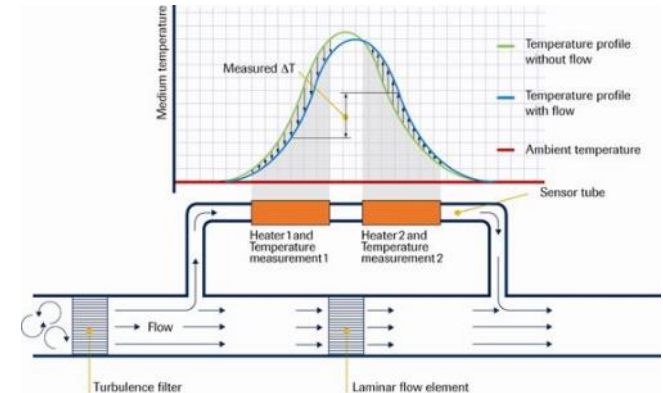
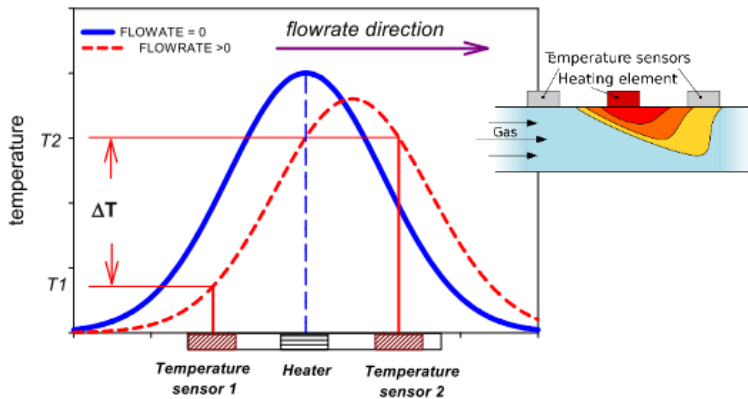
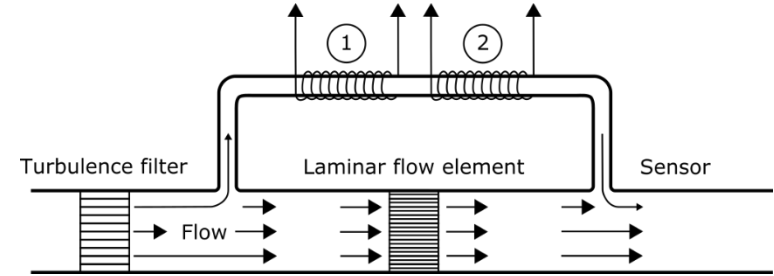
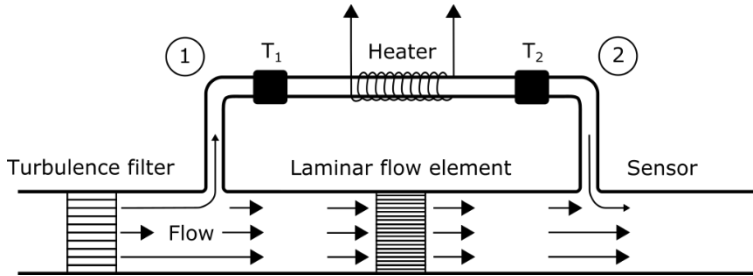
Known manufacturers



❖ CTTMFs (Capillary Type Thermal Mass Flow Meters)

❖ 2 technologies

assumption $\frac{\dot{m}_{capillary}}{\dot{m}_{main tube}} = cst$



Temperature rise flowmeter

$$\dot{m} = cst_T \cdot \Delta T$$

cst_q, cst_T depends on gas nature

Rate loss heat flowmeter

maintaining $\Delta T = cst$

increase rangeability

$$\dot{m} = cst_q \cdot q$$

Measurement techniques

Direct Gravimetric technique

Not accurate : hydrogen mass is low compared to system mass

Direct Volumetric technique

Necessitate very big volumes controlled in temperature

Flow integration technique

Mass flow technique

The most popular direct mesasure

depends on fluid nature

Volume flow technique

Can be very accurate or poor

Not direct measure need pressure, T

The hydride tank characteristics



MAHYTEC
Innovative Hydrogen Solutions



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

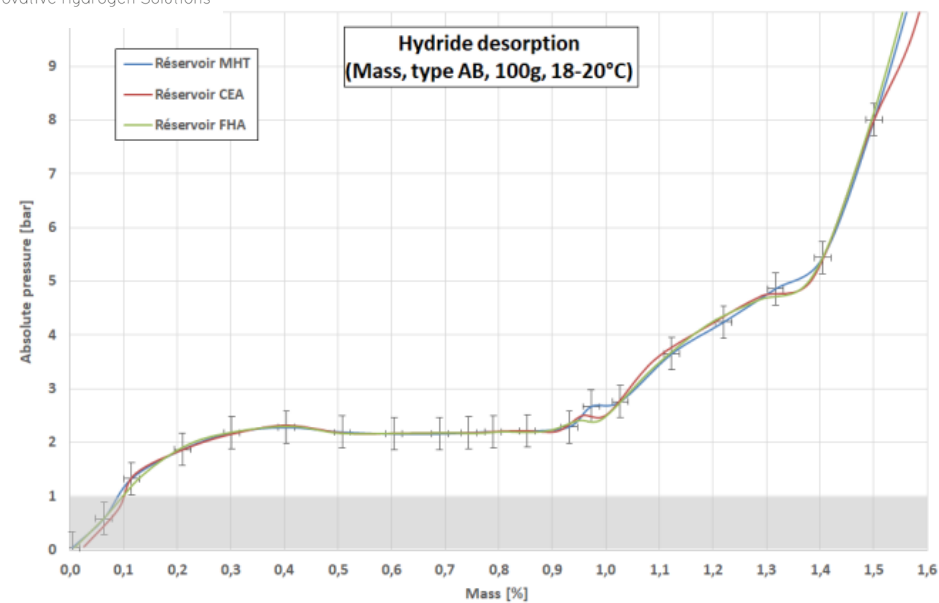
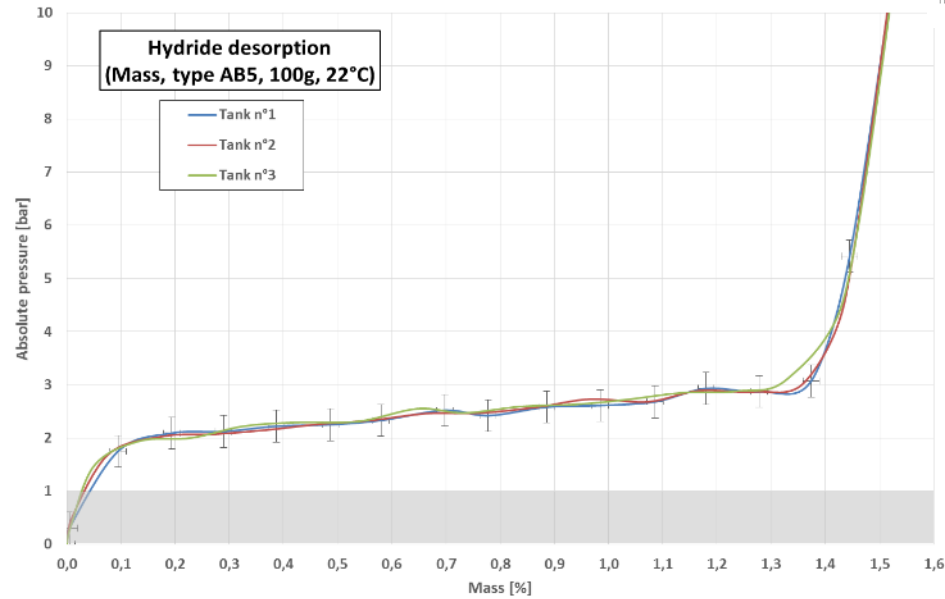


The two hydrides tested

AB₅ type



AB type



Measured by the weight method



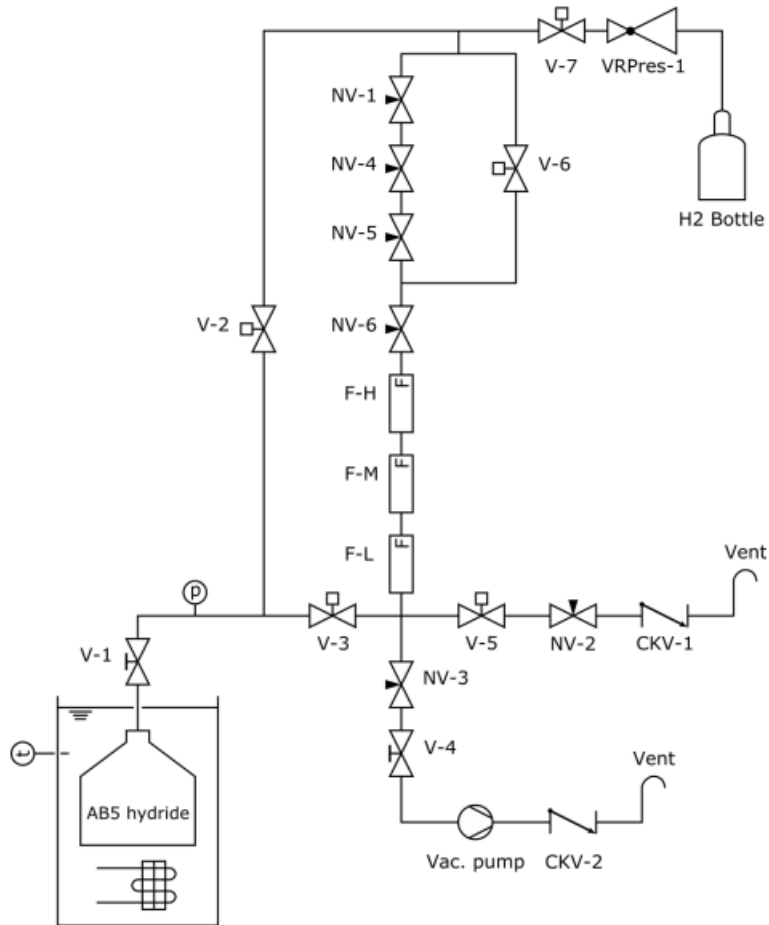
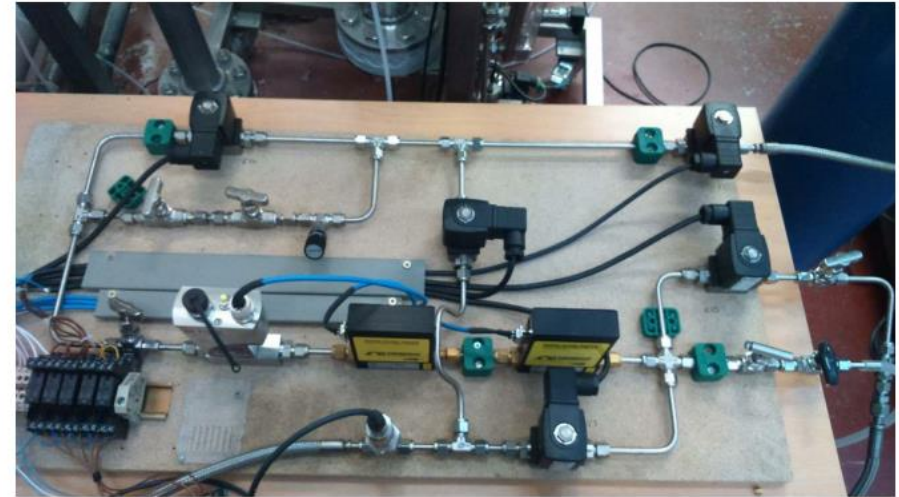
Characteristics of device:
Scale: max 750 g, e = 0.01 g, d = 0.001 g
Digital pressure gauge: EM: -1 ... 30 bar, error: ± 0.2%

Condition test:
Loading: $P_{\text{loading}} = 10 \text{ bar}$ and $T_{\text{loading}} = 22 \text{ °C}$
Unloading: $T_{\text{unloading}} = 22 \text{ °C}$

Properties comparison

	H capacity	PCT	Activation	Impurity Effects	Cyclic Stability	Ease of manufacture	Pyrophoricity	Cost
AB ₅	0	+	+	+	+	+	0	0
AB	0	+	-	-	-	+	+	+

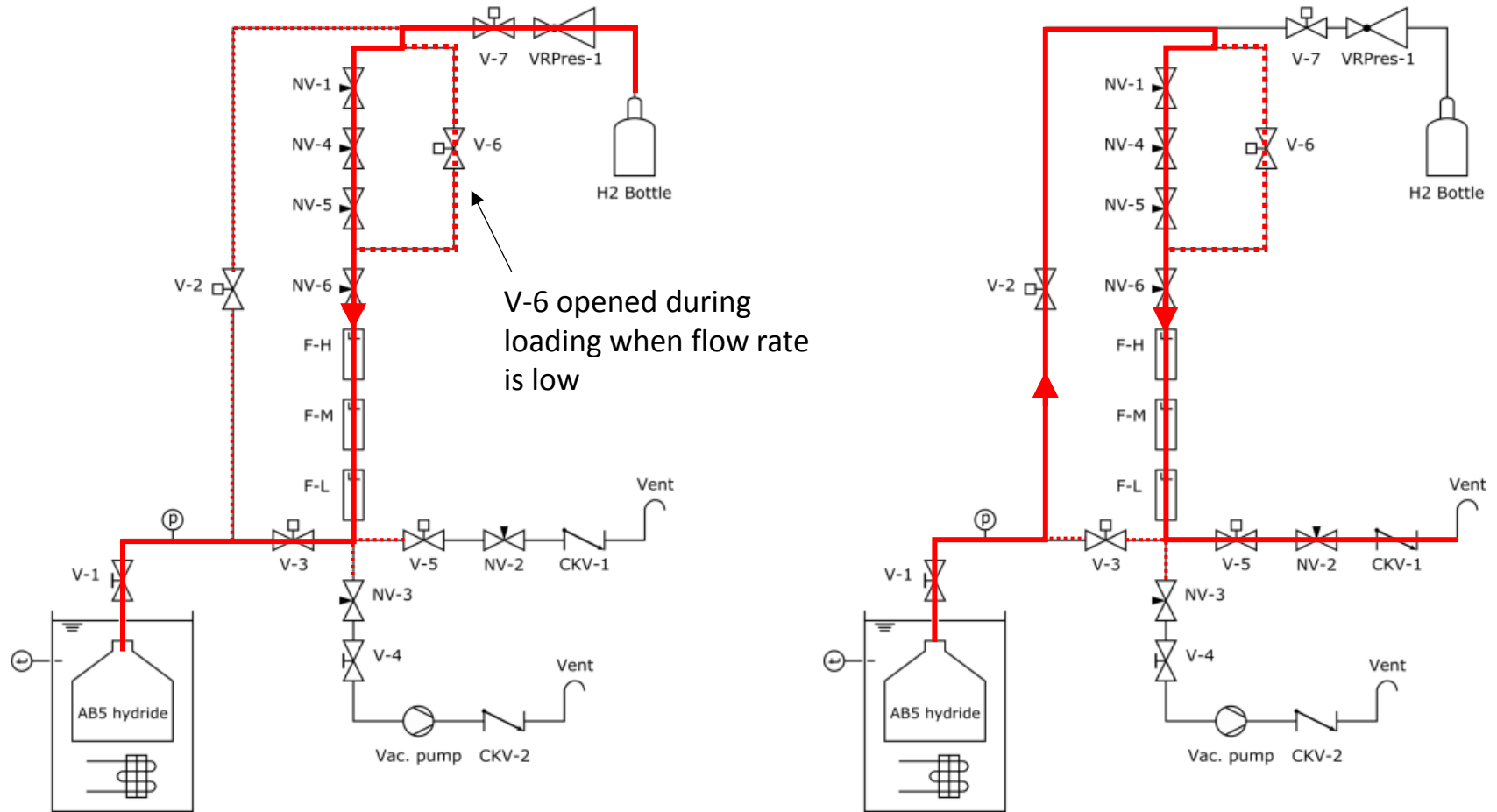
First installation for AB₅ test



FUNDACIÓN PARA EL
DESARROLLO DE LAS NUEVAS
TECNOLOGÍAS DEL HIDRÓGENO
EN ARAGÓN

Advantage : 3 mass flow, larger range (but expensive)

Drawback : no mass flow control

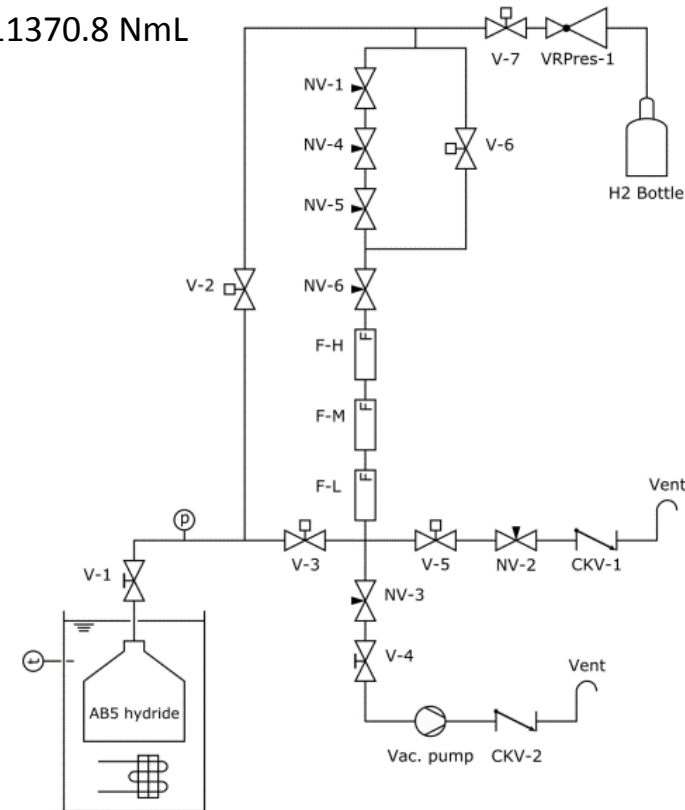
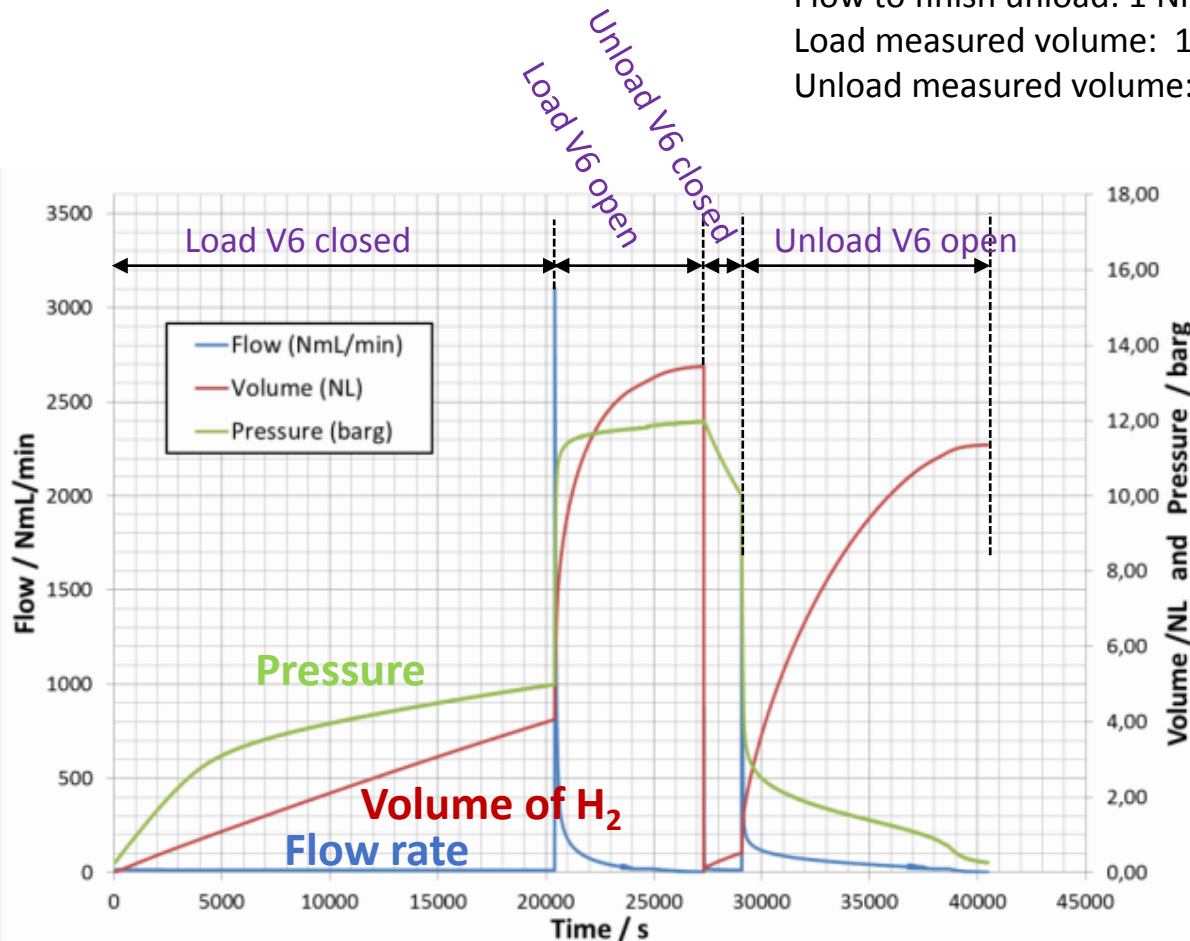


V-6 opened during loading when flow rate is low

Examination of one test

Test 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



FHA results – AB₅ tank

Pload=12 barg
Punload=0 barg

	Test no. 1	Test no. 2	Test no. 3	Test no. 4	Test no. 5	Test no. 6
Température (°C)	22	22	22	22	35	22
Load P V-6 opening (bar)	5	5	5	5	5	5
Unload P V-6 open (bar)	8	5.5	10	11.9	11.9	5.2
Load stop mass flow Nml/min	1	1	1	1	1	1
Unloas stop mass flow Nml/min	0.5	1	1	1	1	1
Volume (load) Nml	15214,9	15488	14947,6	15329,5	13450,6	15287,7
Volume (unload) Nml	11917,33	13491	13230,2	12312,2	11370,8	12123,8
Load/Unload Deviation %	+21.7	+12.9	+11.5	+19.7	+15.5	+20.7
Load MAHYTEC Deviation %	-9,44	-7,81	-11,03	-8,75	-19,94	-9,00
Unload MAHYTEC Deviation %	-29,06	-19,70	-21,25	-26,71	-32,32	-27,83

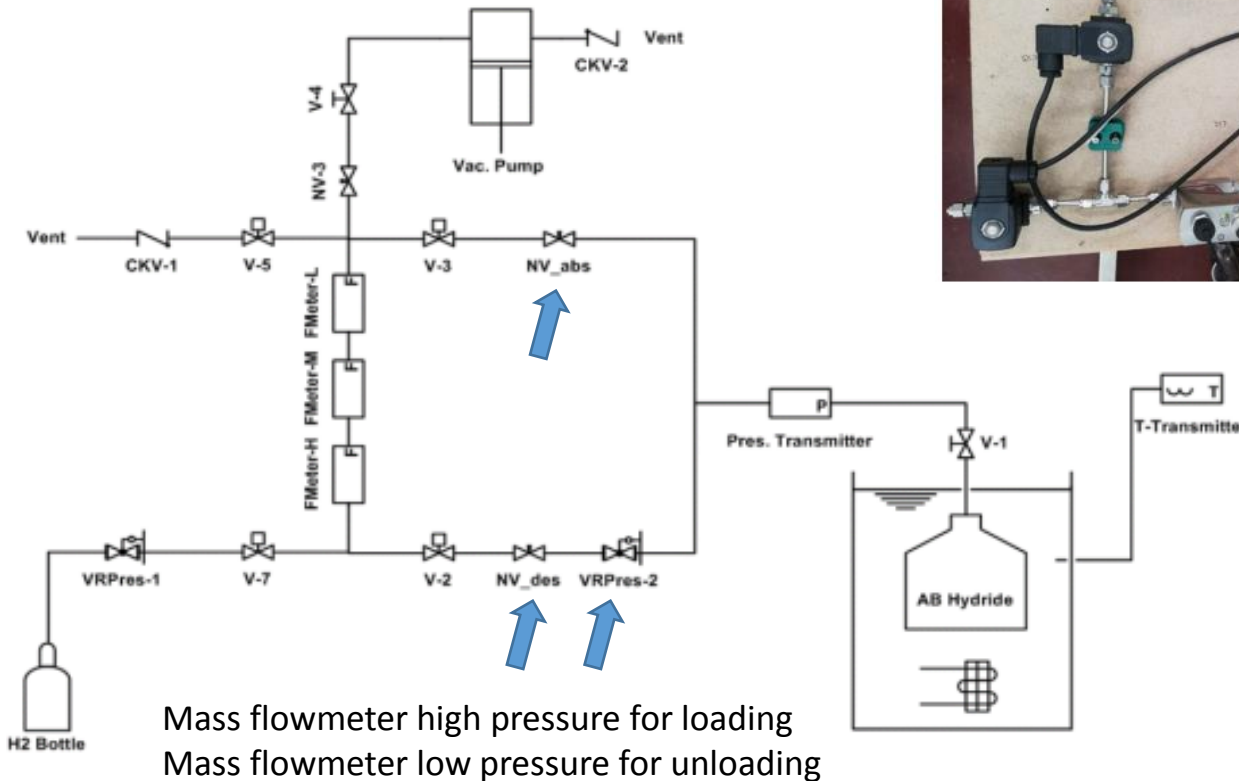
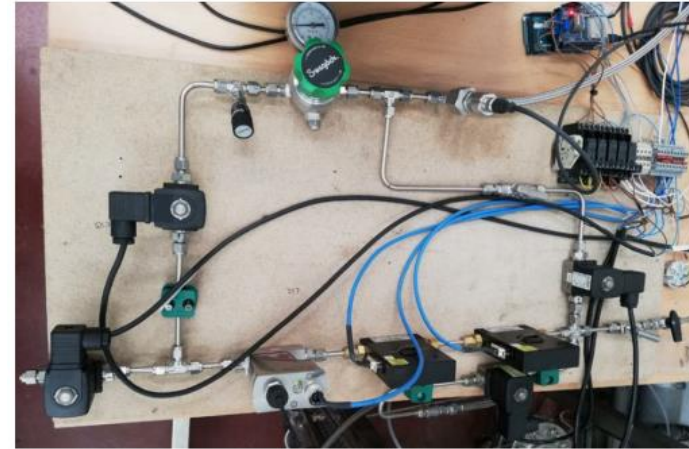
NV-2, NV-
4 NV-5
closed a
bit

NV-2
closed

Conclusions

- ✓ High di-symmetry of load and unload measures
- ✓ Underestimation compare to the Mahytec capacity measure
depending on the adjustments, from -7% to -30% difference
- ✓ Adjustment of needle valve opening is difficult (iterative)
- ✓ Despite the use of needlevalves, there are overflows at each stage
- ✓ Needle valves oblige to cut the load into two parts (V6 opening) with
overflow at each V6 opening
 - ➔ 1 overflow at loading, 2 overflows at unloading
- ✓ Capacity measured is dependant on needle valves ajustements and
switching pressure (for V-6 valve) !

Second installation for AB test

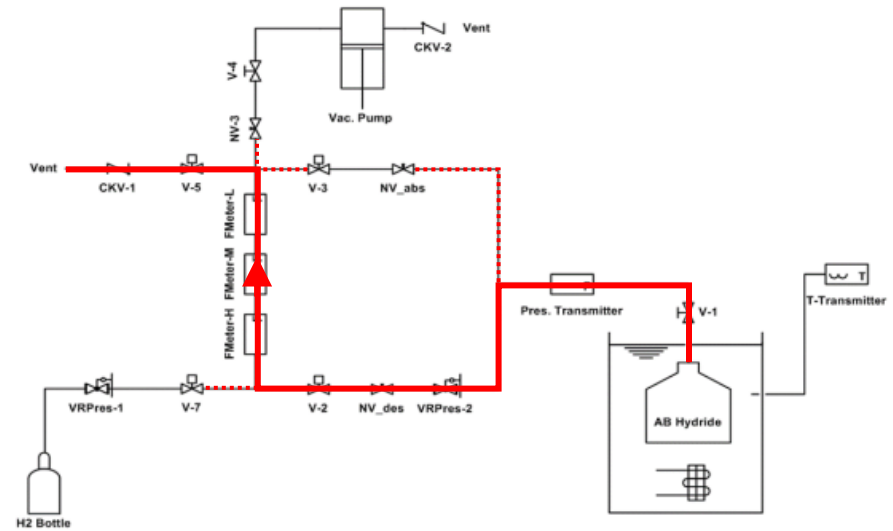
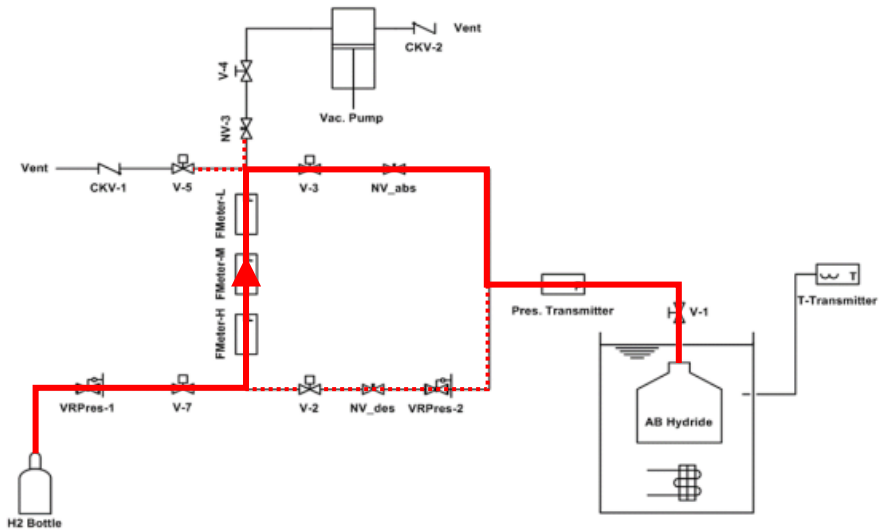


FUNDACIÓN PARA EL
 DESARROLLO DE LAS NUEVAS
 TECNOLOGÍAS DEL HIDRÓGENO
 EN ARAGÓN

New :

- Needle valve (NV_abs) after flowmeter in order to maintain P more constant on flowmeter
- Pressure regulator valve (VRPres-2) added for desorption before a needle valve (NV_des)

First installation for AB test

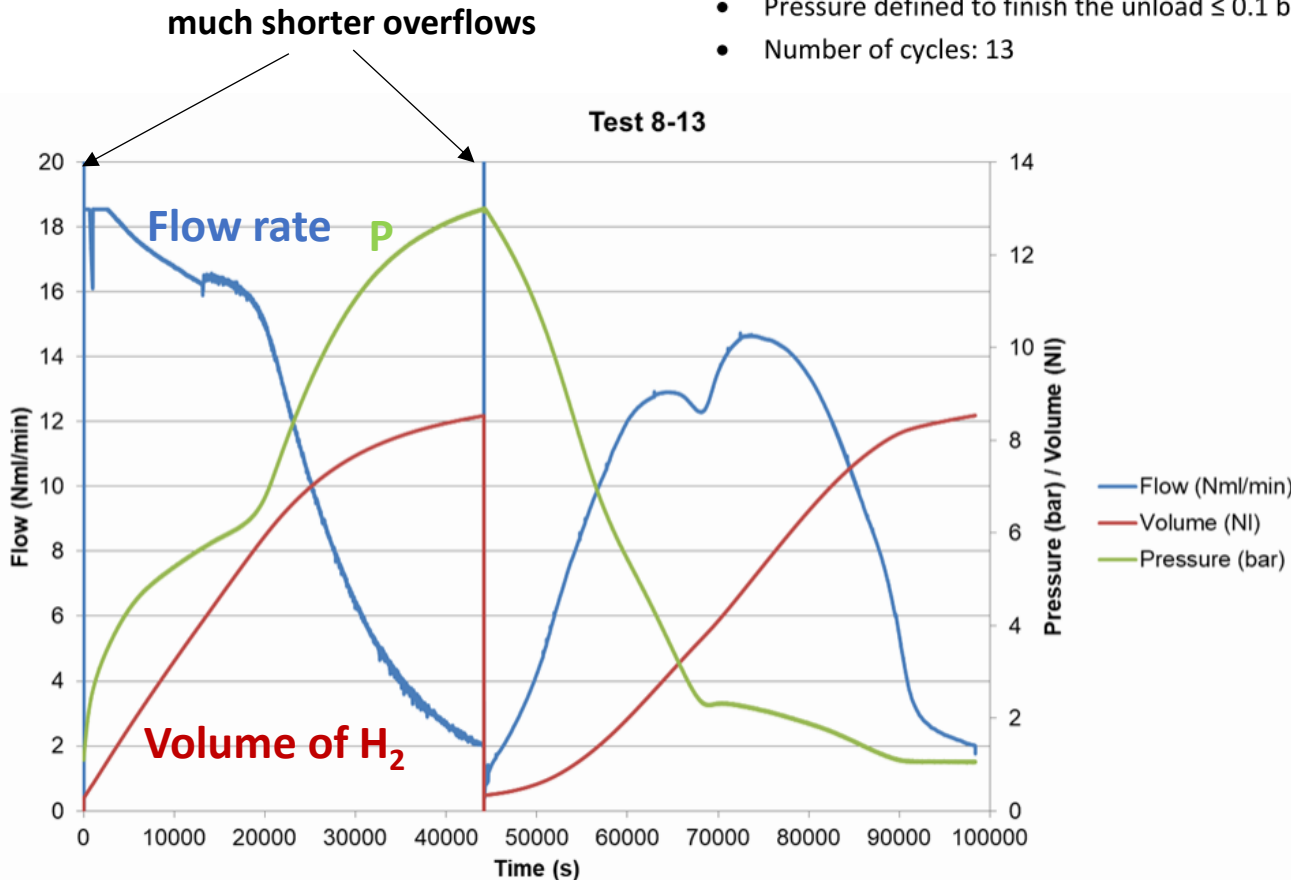


Examination of one test

The test was performed under the following conditions:

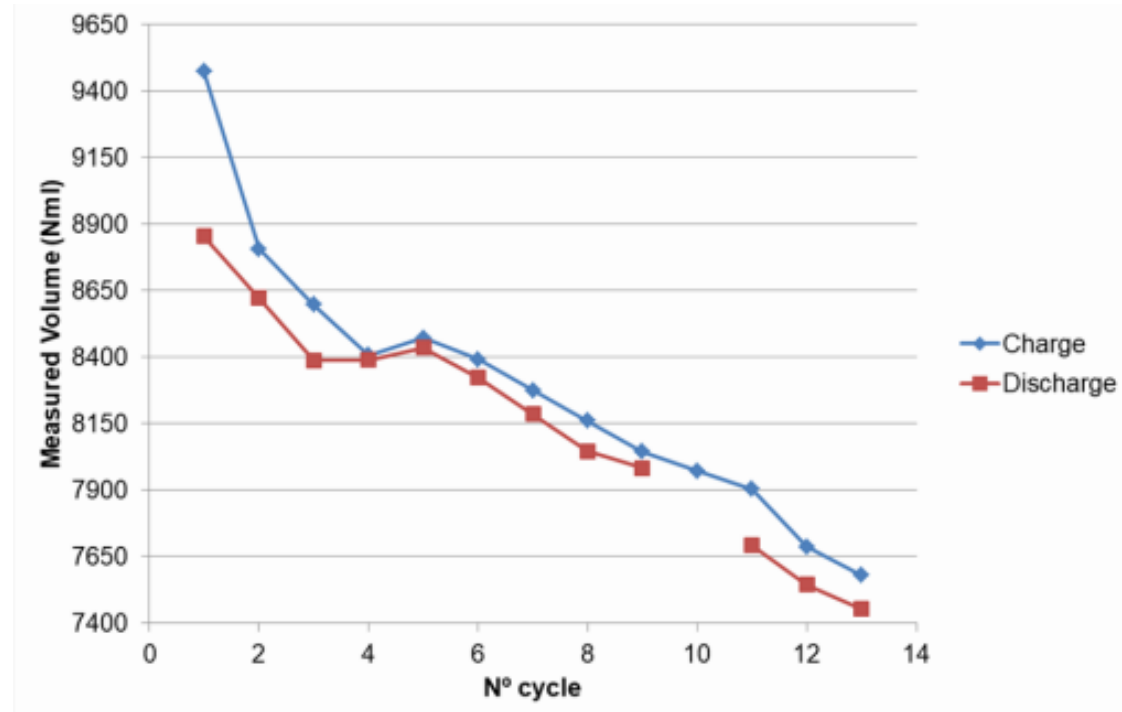
- Temperature: 22 °C
- Inlet Pressure: 14.5 barg (15.5 bara)
- Flow to finish load: 2 NmL/min
- Pressure defined to finish the load ≥ 11 barg (12 bara)
- Flow to finish unload: 2 NmL/min
- Pressure defined to finish the unload ≤ 0.1 barg (1.1 bara)
- Number of cycles: 13

Both the pressure and the flow criteria have to be accomplished



Results on 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

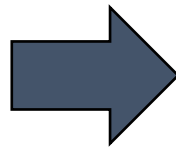


Much closer values for loading and unloading

**Significant decrease of capacity : behavior of the AB hydride ?
or a malfunctioning of pressure reducer VRPres-1**

The test bench have been modified for the project :

- remove the 2cd mass flow
- replace the check valve by simple valves
- introduce a length before the mass flow in order to have a better establishment length
- change the PRD to 15 bars



CySHY test bench



The 10 g/h mass flow has been re-calibrated to 800 Nml/min.

Gas panel

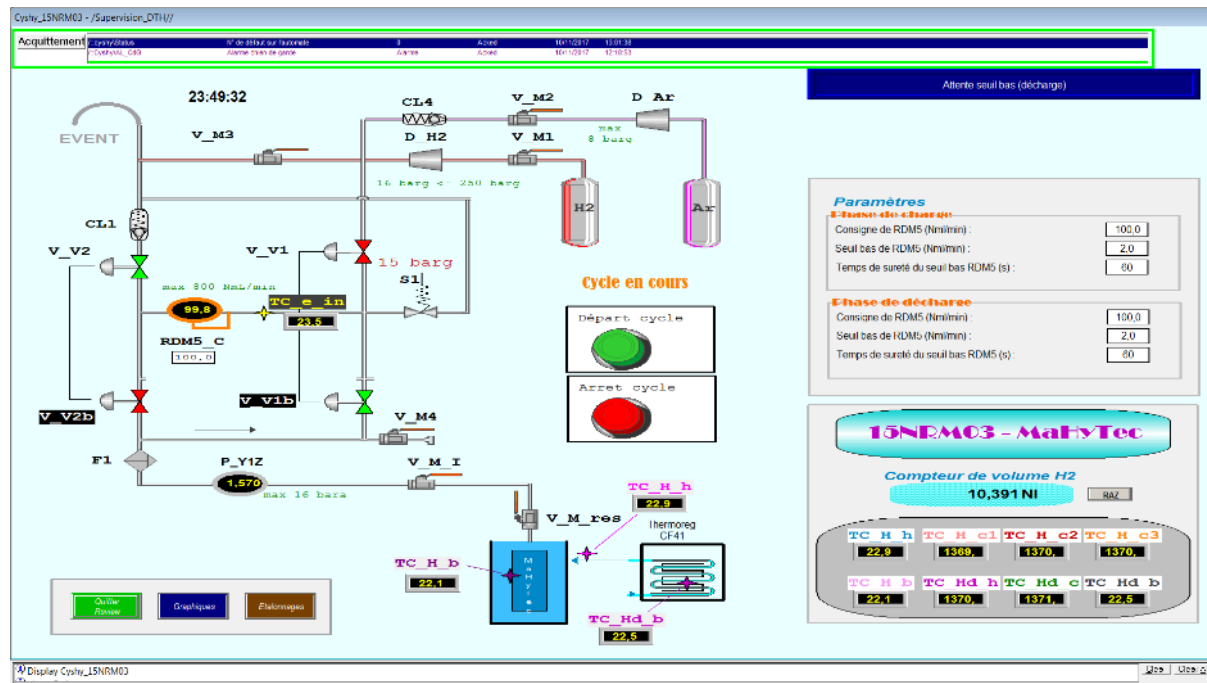
Water bath in which the hydrogen tank is installed

Thermoregulator

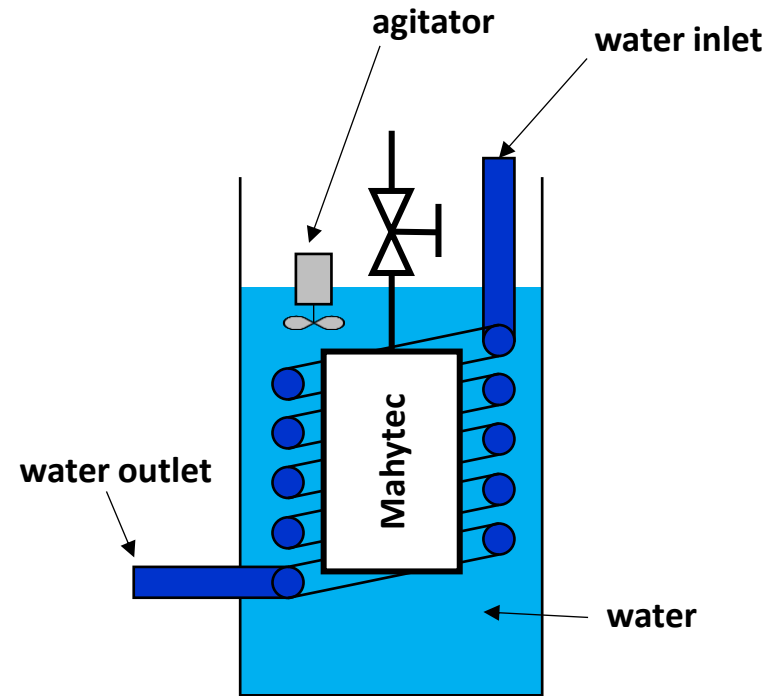
Programmable automaton (Allen Bradley)



Synoptic (RS-View)

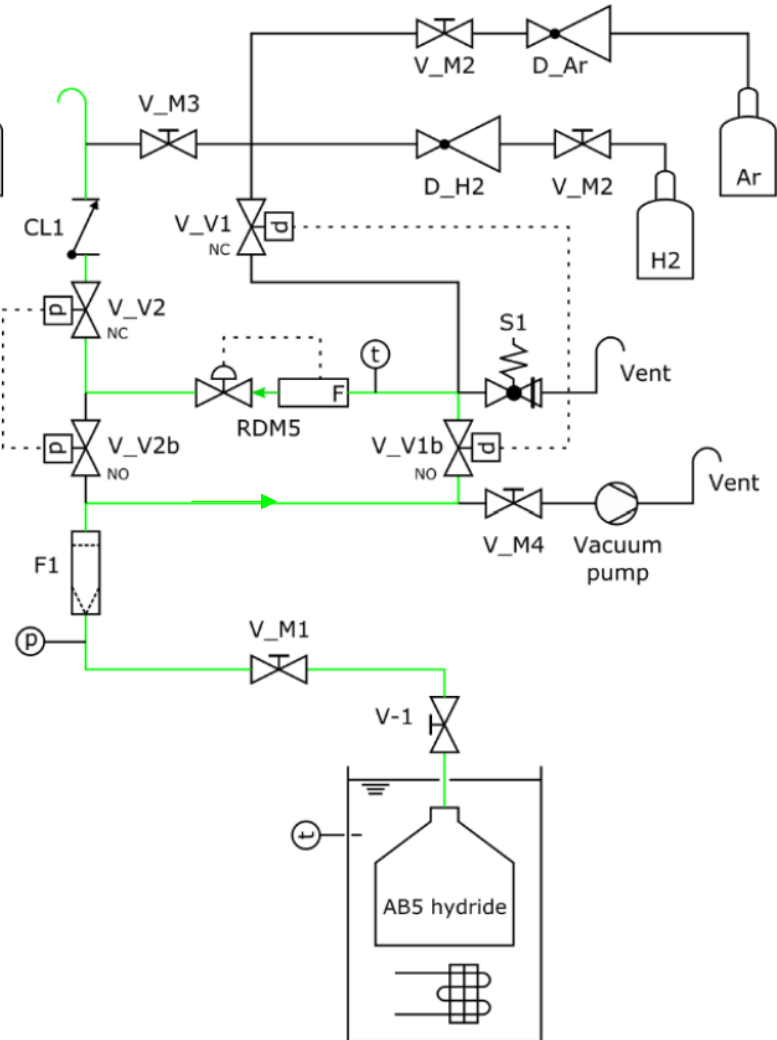
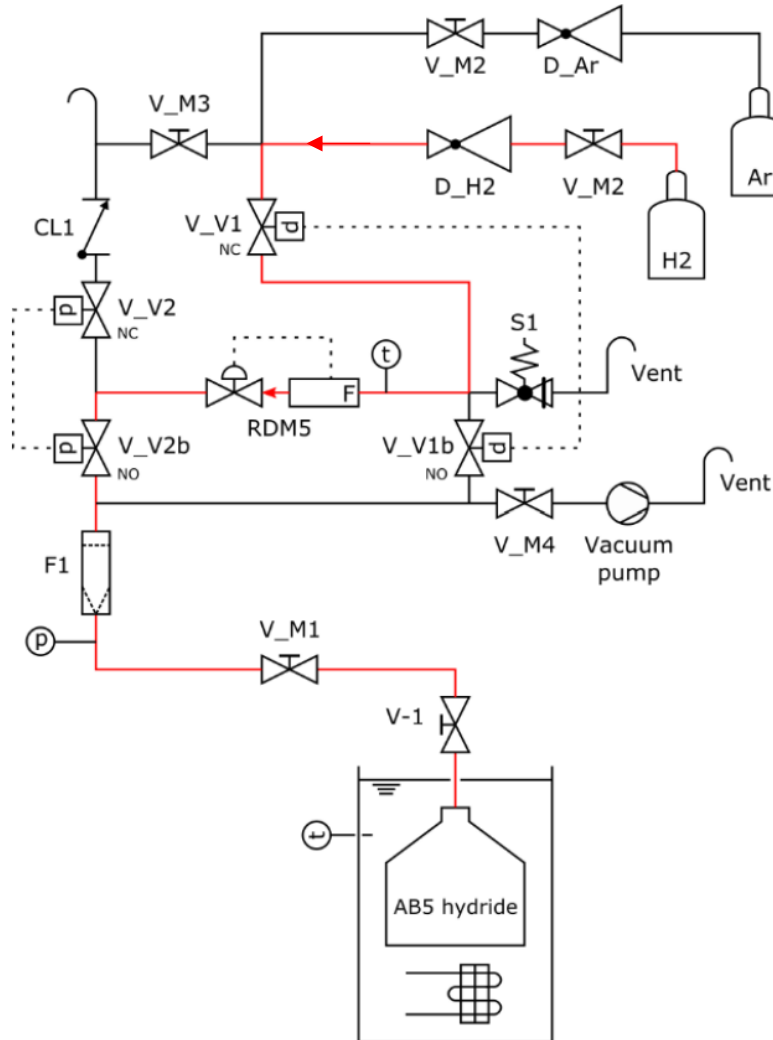


thermocouple

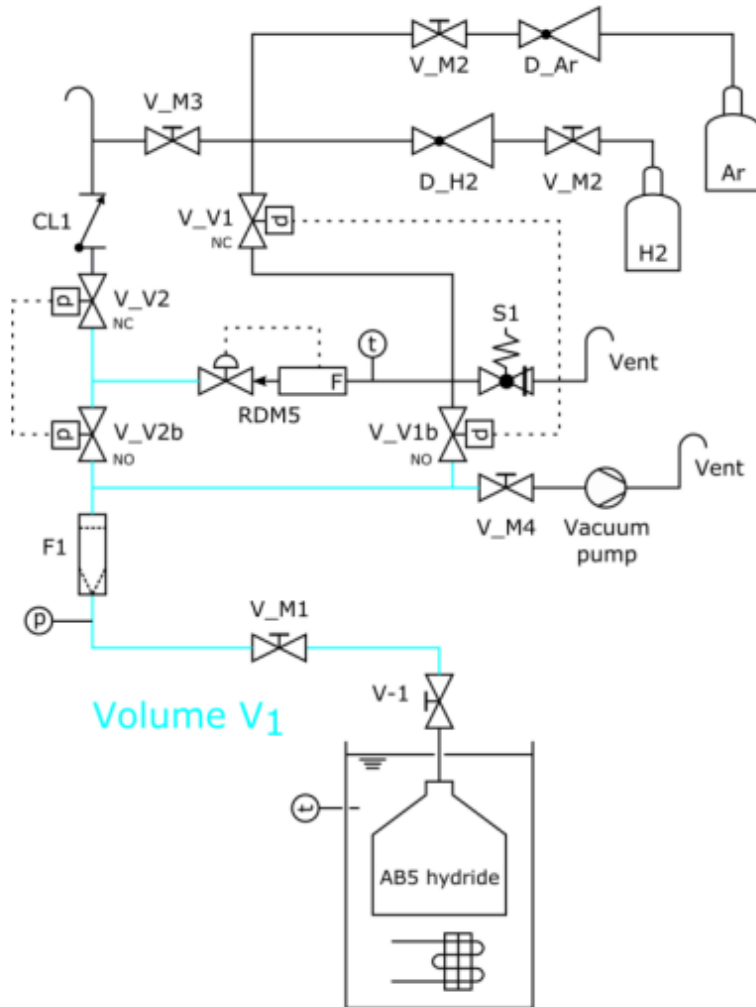


Loading

Unloading



Dead volume correction



**V1 volume is counted by mass flowmeter but is not entering in the tank
→ has to be withdrawn from measure**

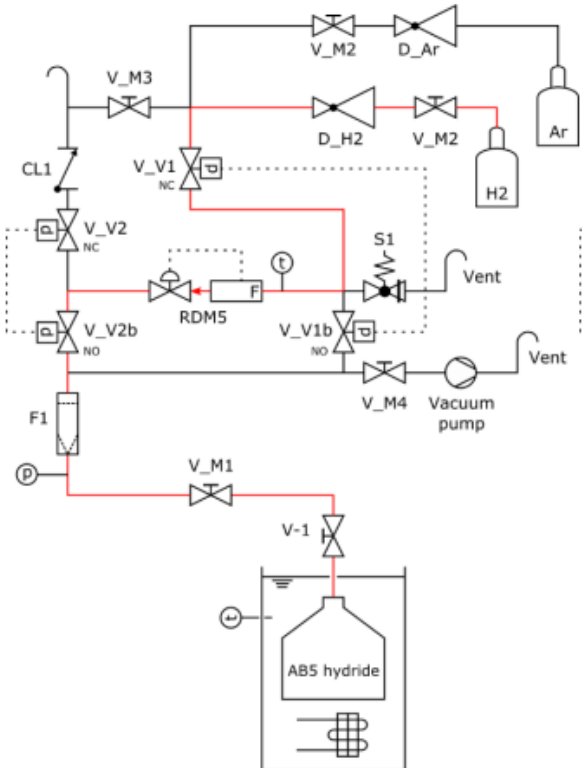
Test protocol

Initial conditions

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

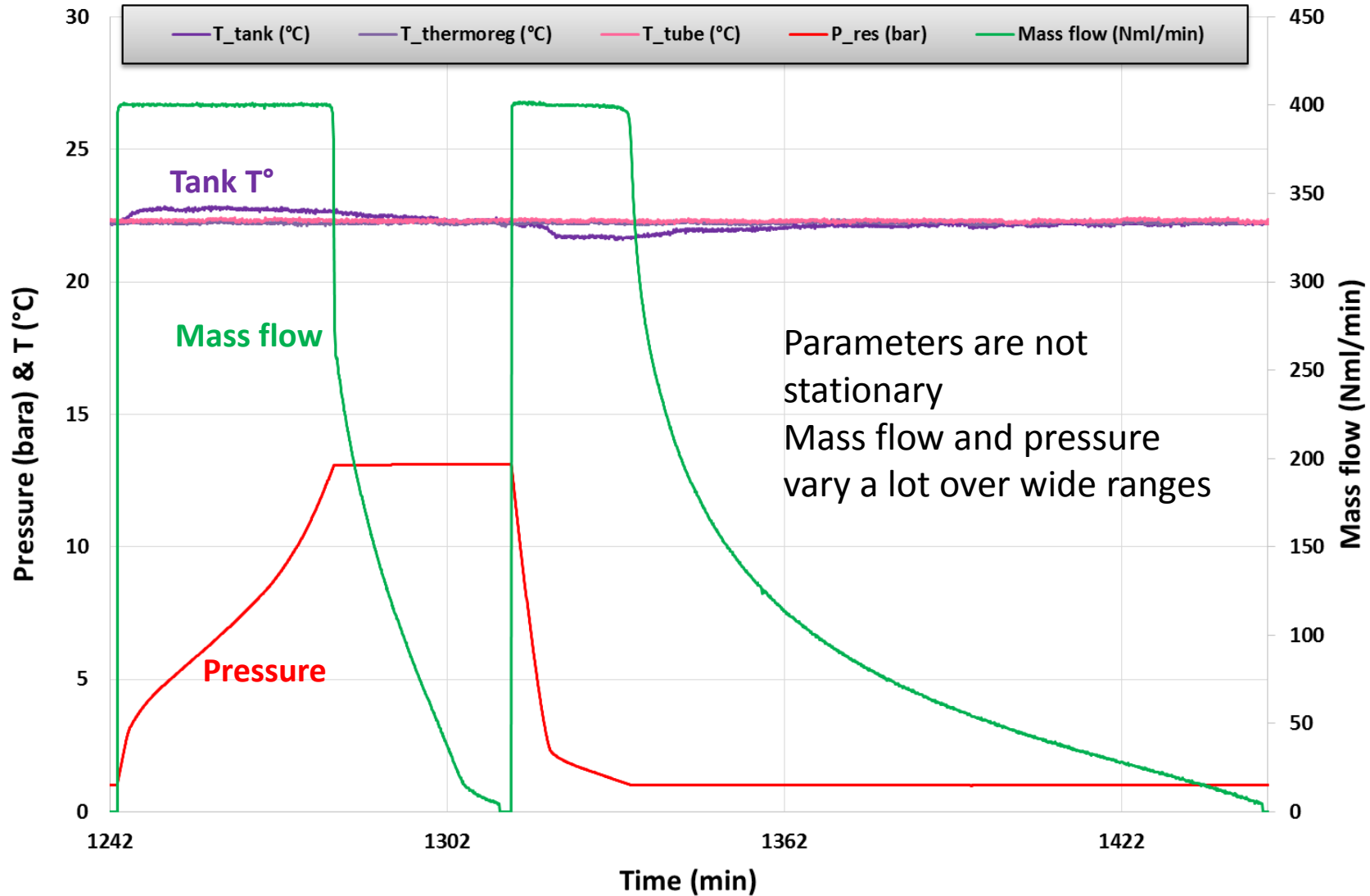
Adjustable parameters

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	in order to avoid overflow	
	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		
Unload	8	RDM5_C = 0		
	9	Wait : 60 s		
	10	Ouverture V_V2		
	11	RDM5_C = 0,1	in order to avoid overflow	
	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		

Experiment at 400 Nml/min : 5th cycle

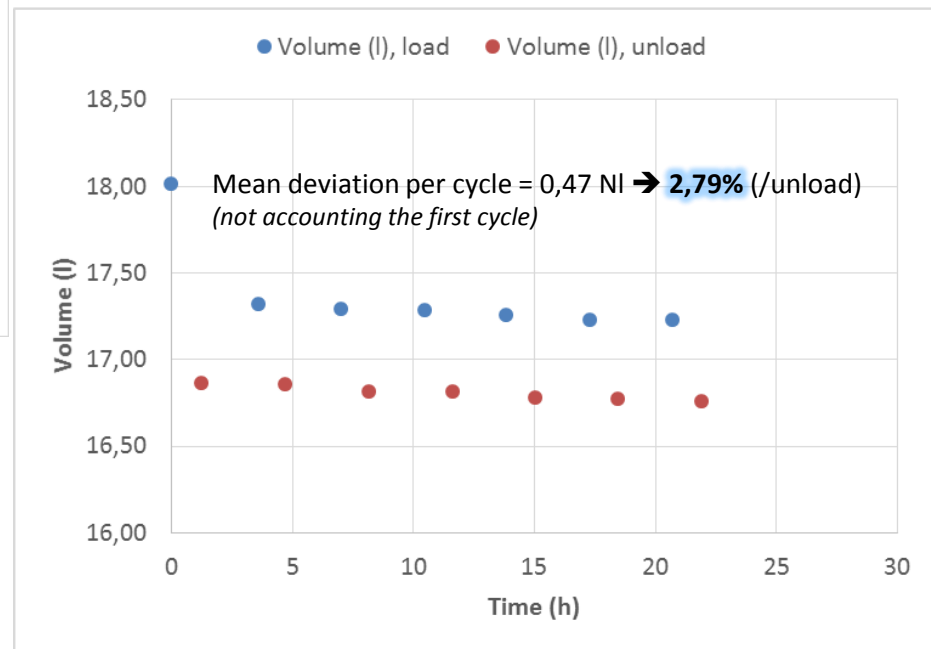
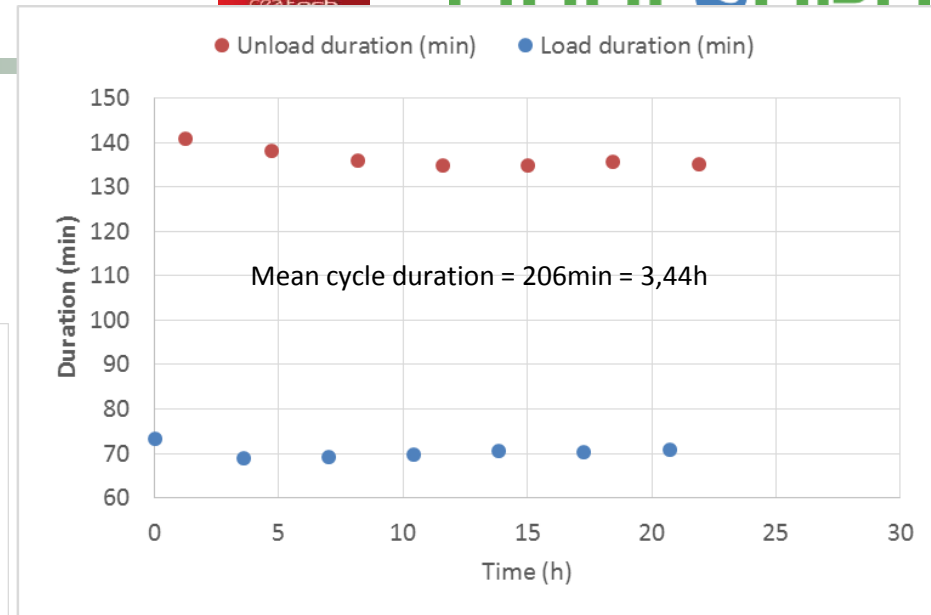
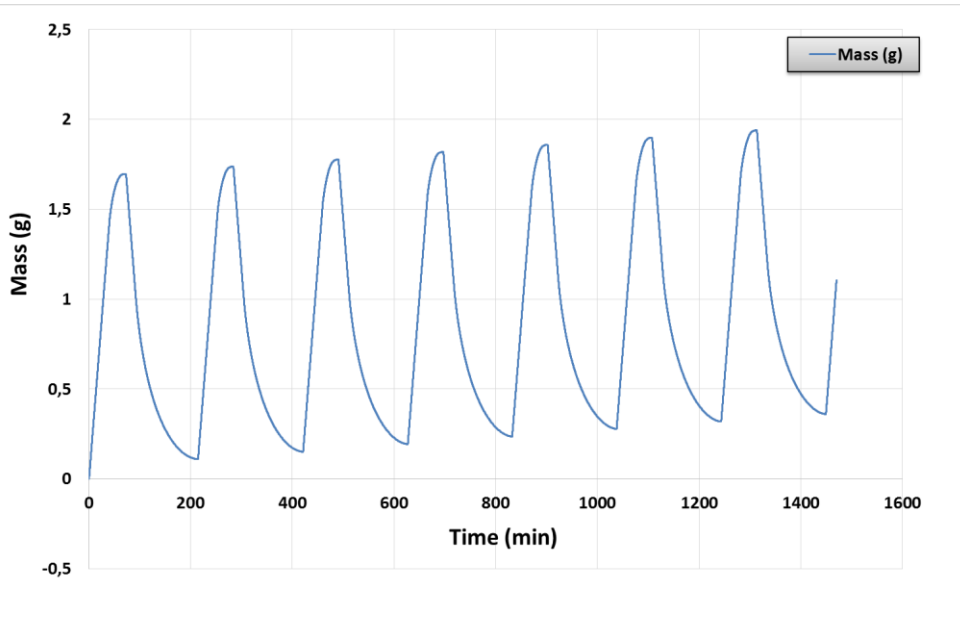


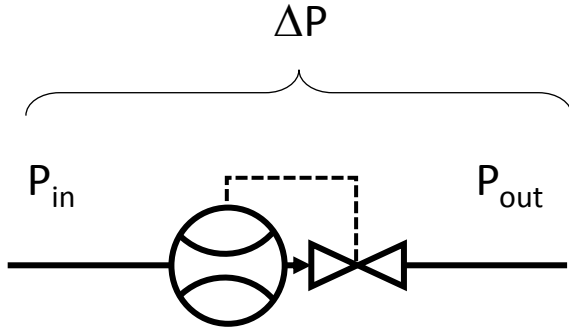
CEA Results – AB₅ tank



Experiment at 400 Nml/h

Cumulated mass

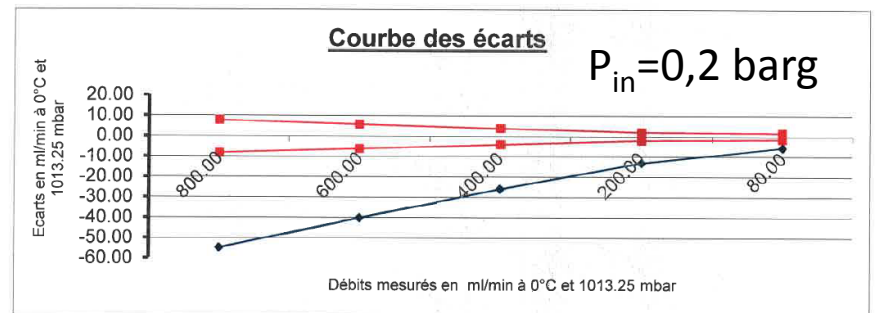
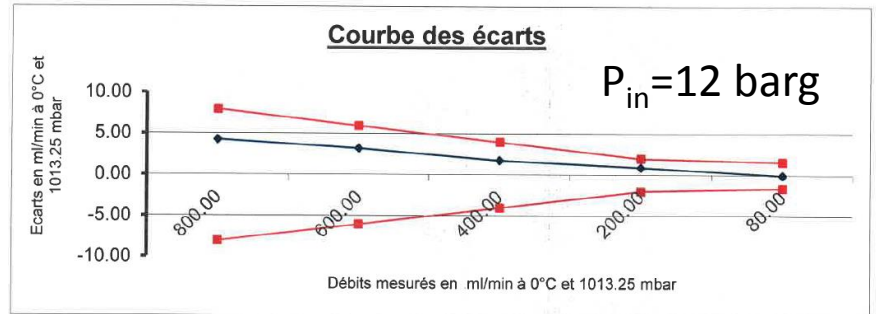
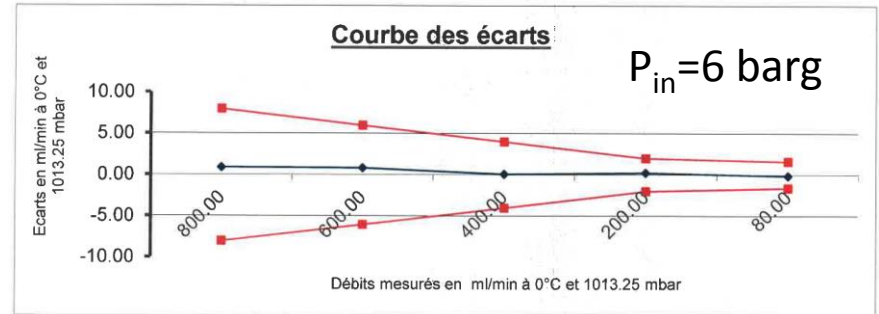




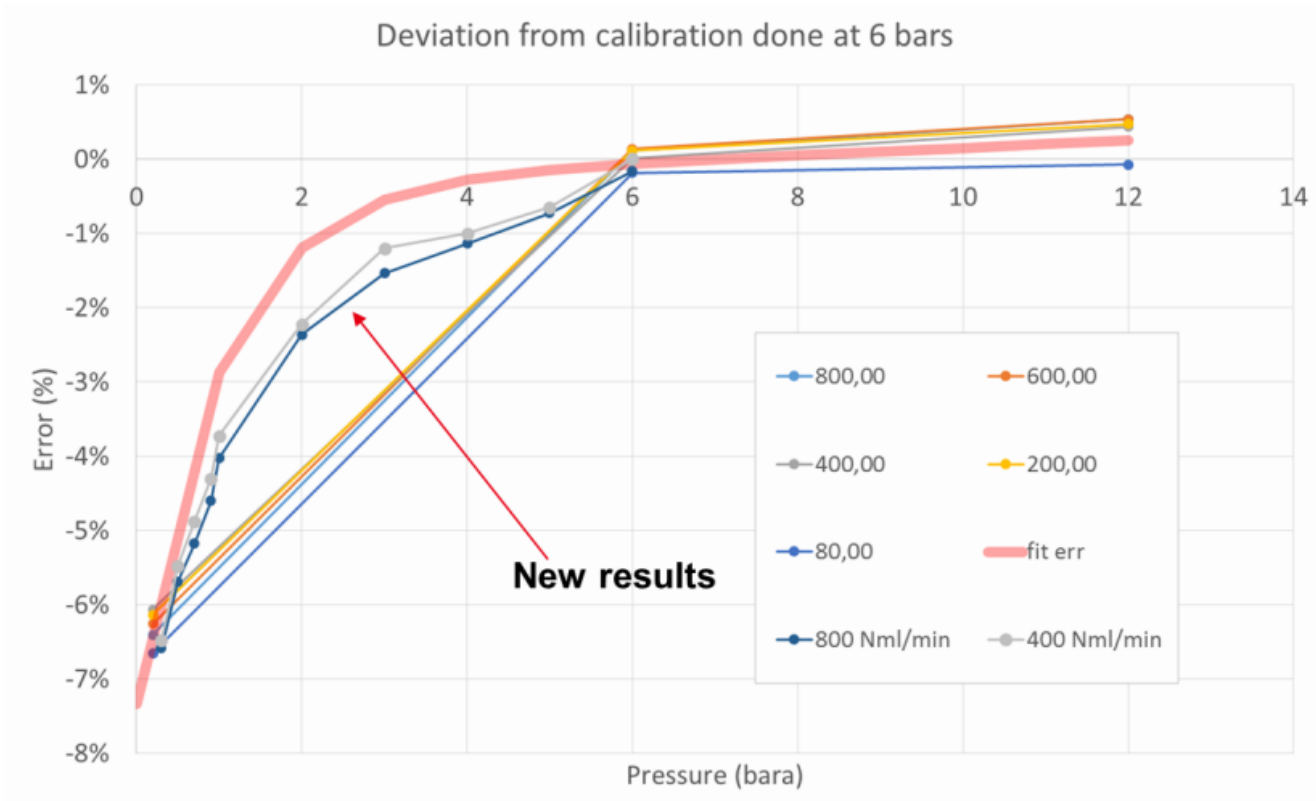
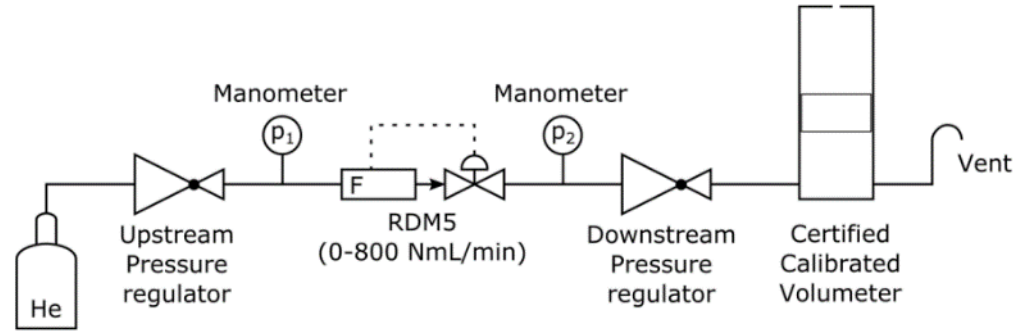
	P_{in} (bara)	P_{out} (bara)
Loading	13,136	P_{tank}
Unloading	P_{tank}	0,985

Problem when P or $\Delta P \approx 0$!!! →

Calibration as proposed by the provider

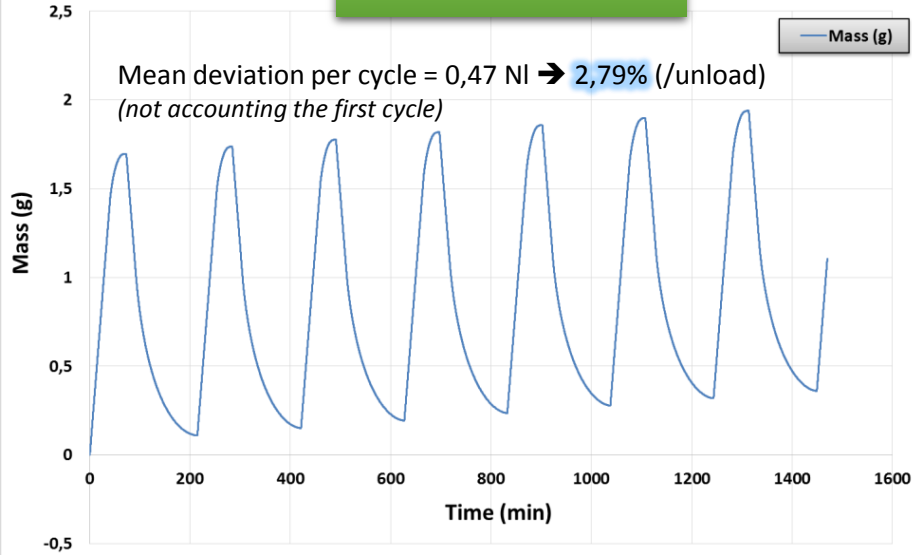


Result of extended calibration

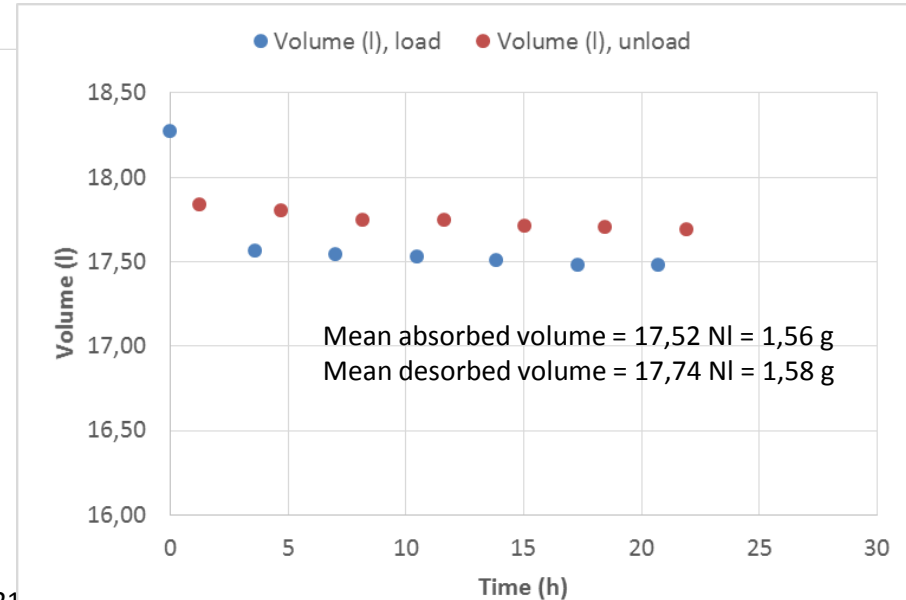
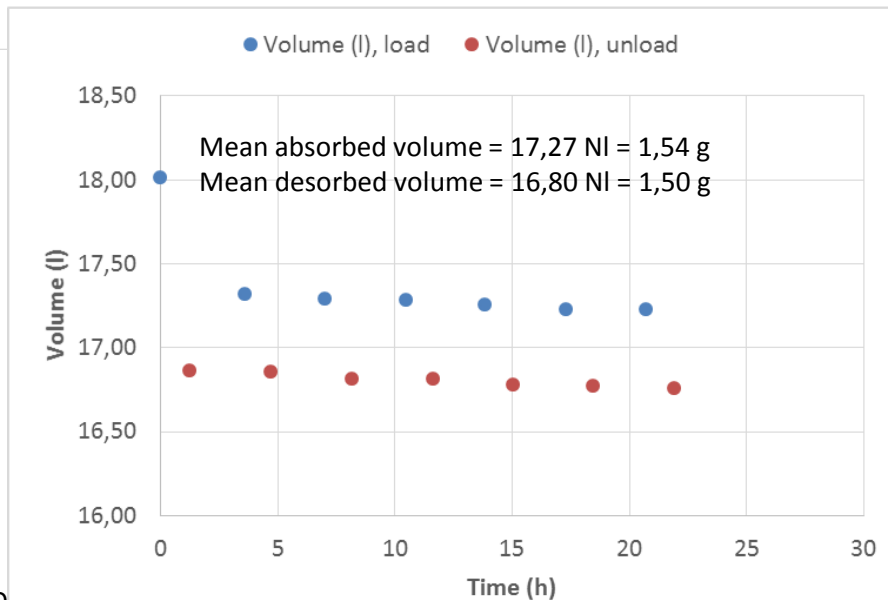
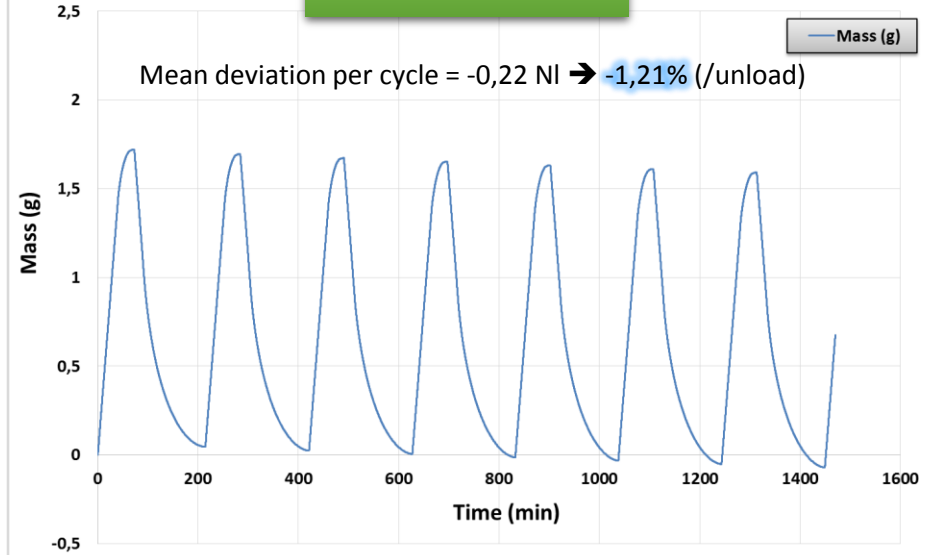


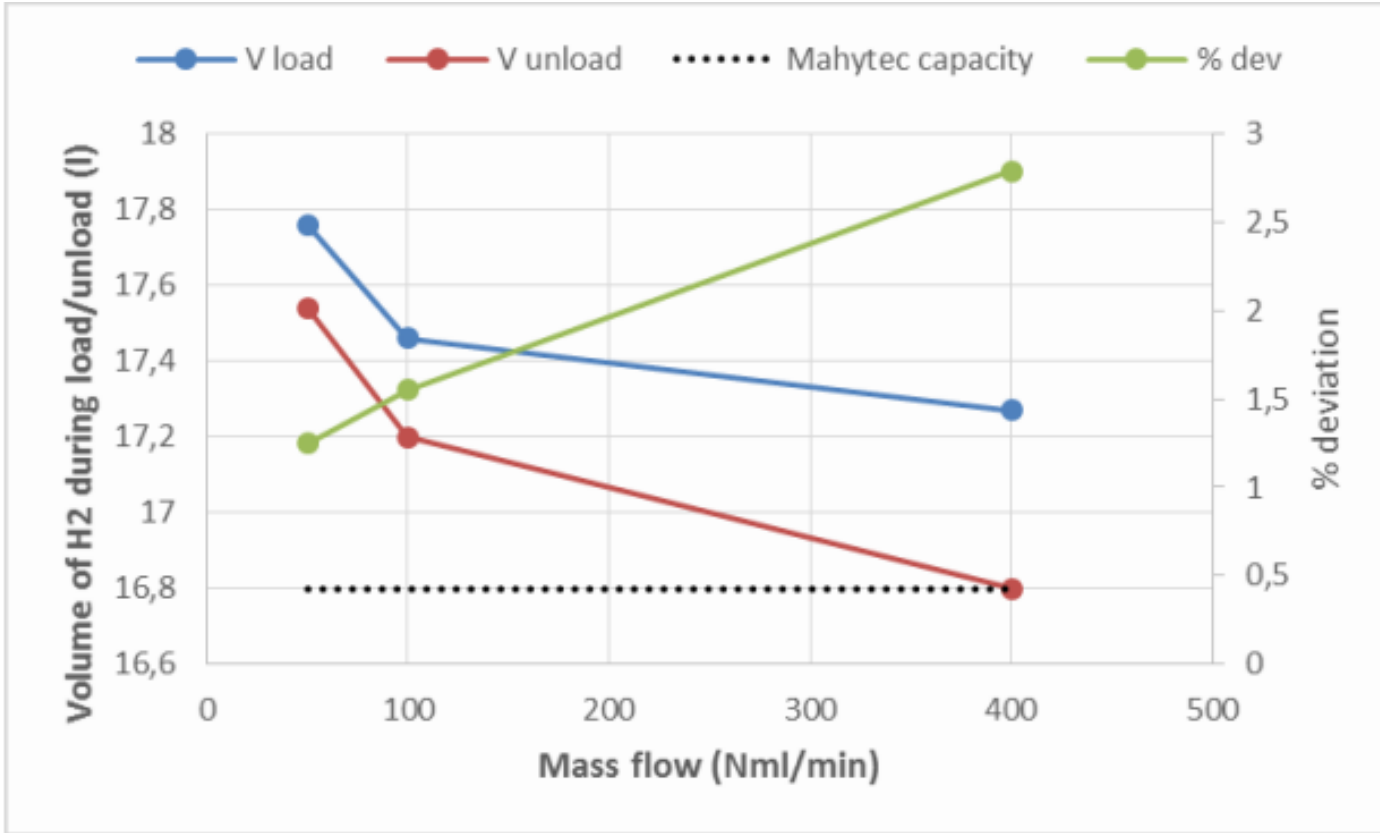
Result of extended calibration

Before correction



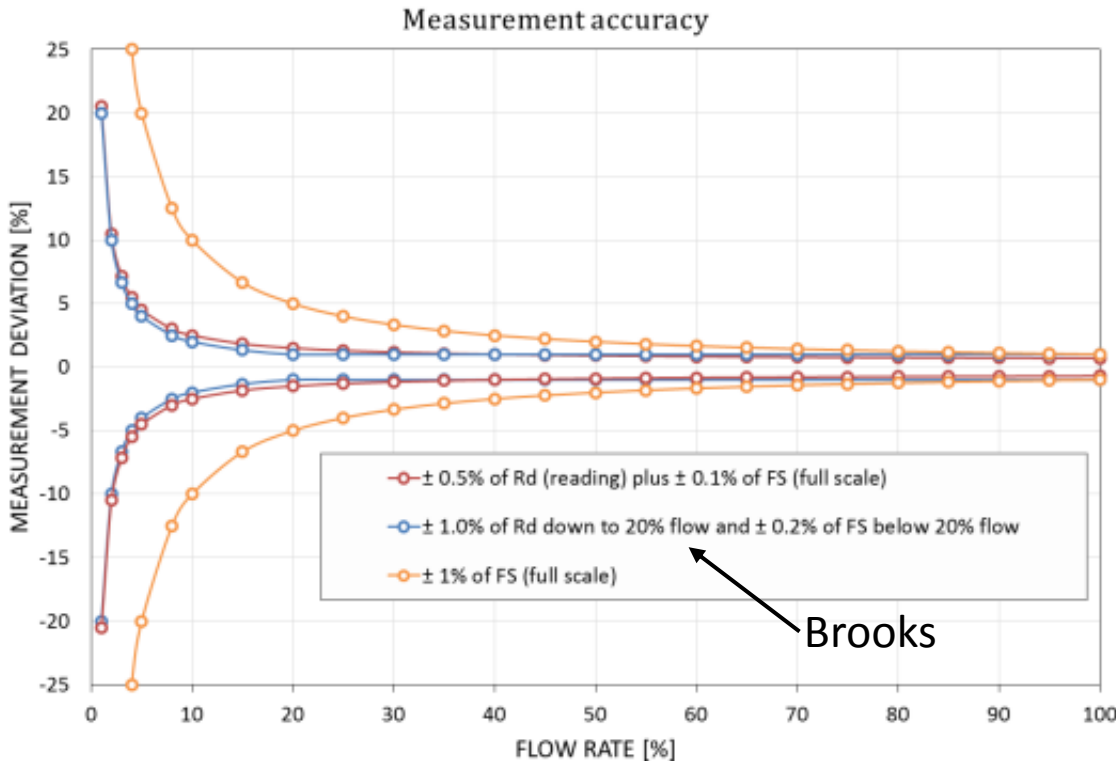
After correction





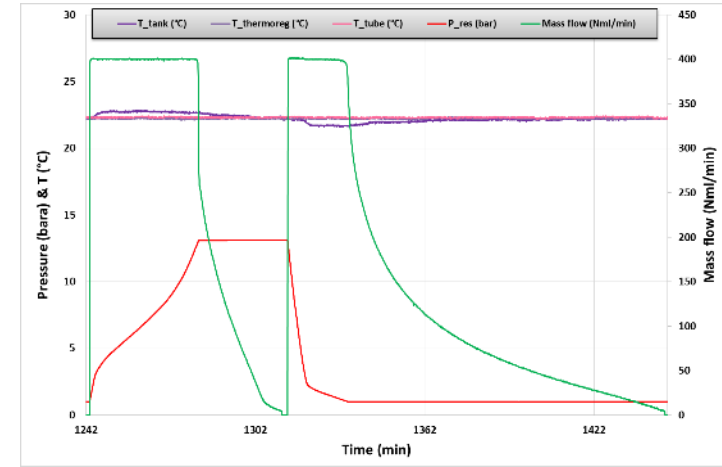
Not too bad compared to Mahytec measurement [0% : 5,7%]

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%

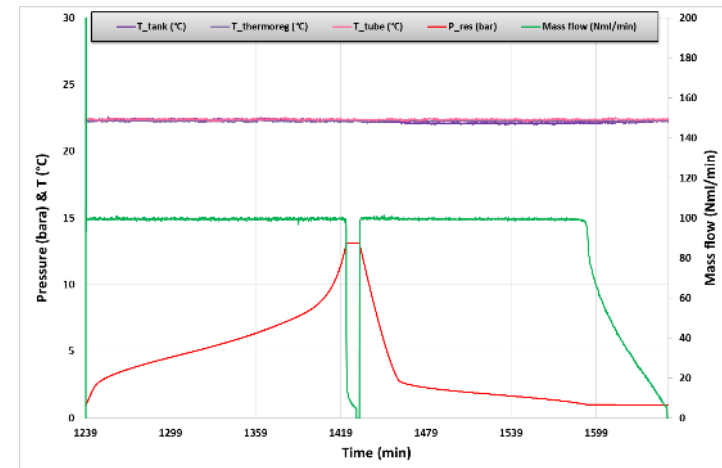


➔ can also explain the difference of capacity measured between loading and unloading

quite di-symmetric loading unloading at 400 Nml/min

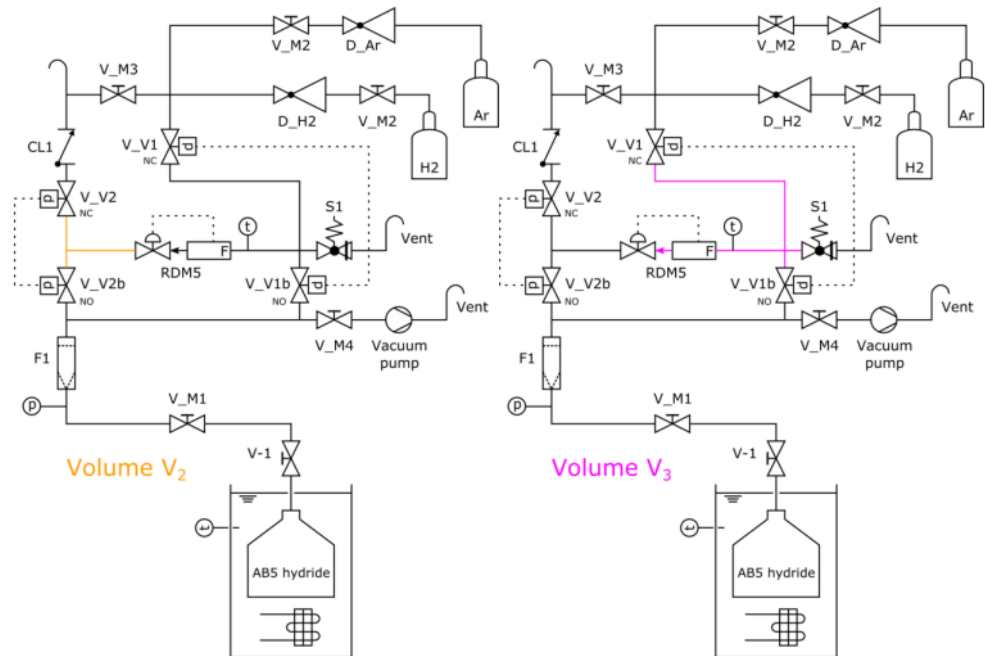


less di-symmetric loading unloading at 100 Nml/min



- Find origin of mass flow measure deviation at low P !?!?
 - ✓ Temperature bias via massflow meter body heating ? (control valve heating ?)
 - ✓ Flow regime change ?
 - ✓ Influence of flow rate piloting valve ? (transient flows...)

- Do finer corrections
 - ✓ Volume V2 and V3
 - ✓ Di-symmetric loading/unloading
 - ✓ Sometimes : overflow
 - ➔ estimate error
 - ✓ Transcient flow regimes :
 - ➔ well time integrated ?



2 points to pay attention

- When using needle valves (NV) for regulating the mass flows

Mass flow vary a lot !!!

➔ reduce this : use pressure regulators in order to pilot constat ΔP on NV

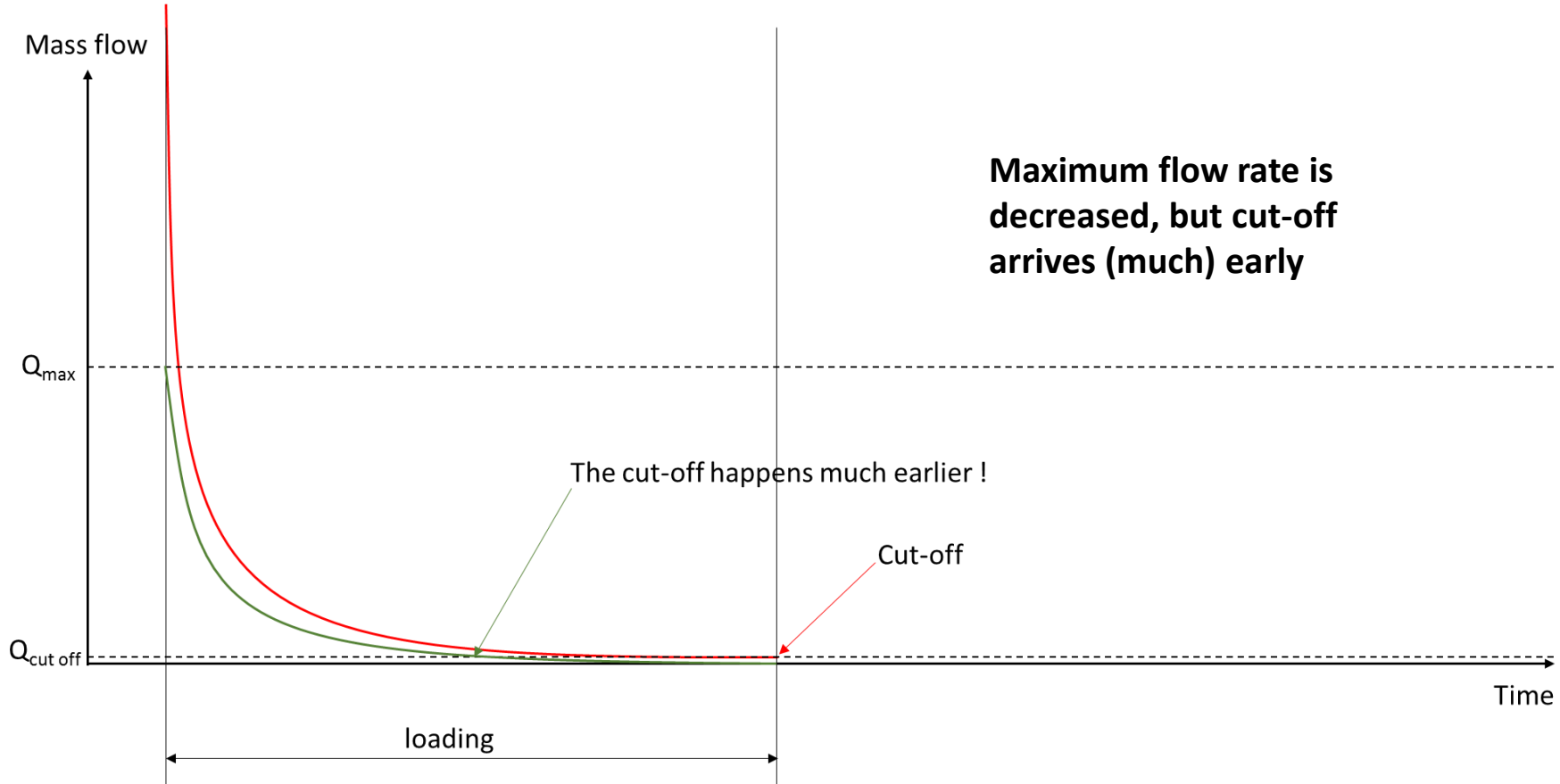
- When using a mass flow meter controller (no NV)

Use a controlled flow rate well in the mass flowmeter range

Deviation when used at low pressure !

➔ avoid this : work near the calibration pressure
or calibrate at two pressures

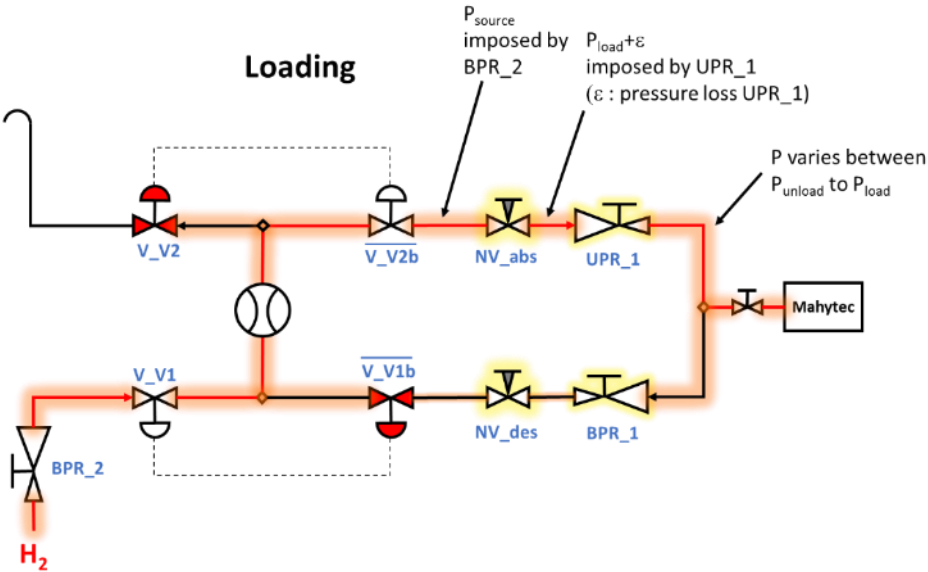
Problem using a needle valve without a pressure regulator



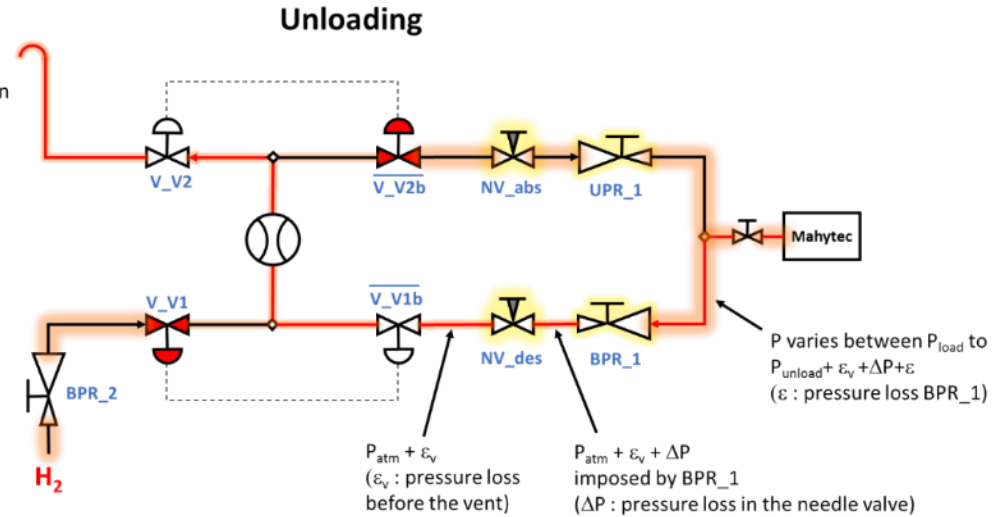
Mass flow through a NV : $\dot{m} = \sqrt{\frac{2 M_{H_2}}{\Lambda RT} S^2 P \Delta P}$ → need to maintain P and ΔP constant

Proposed test bench when using needle valves

BPR Backward pressure regulator
UPR Upward Pressure Regulator
V_Vx Valve
NV Needle Valve



Mass flow works at P_{source}
Needle valve works at P_{source}



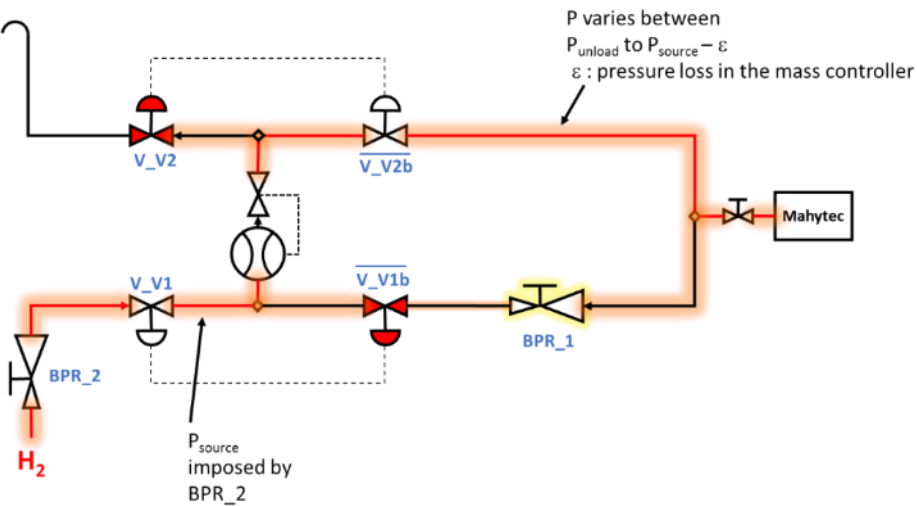
Mass flow works at $\sim P_{atm}$
Needle valve works at $\sim P_{atm}$

Proposed test bench when using mass flow controller

BPR
UPR
V_Vx
NV

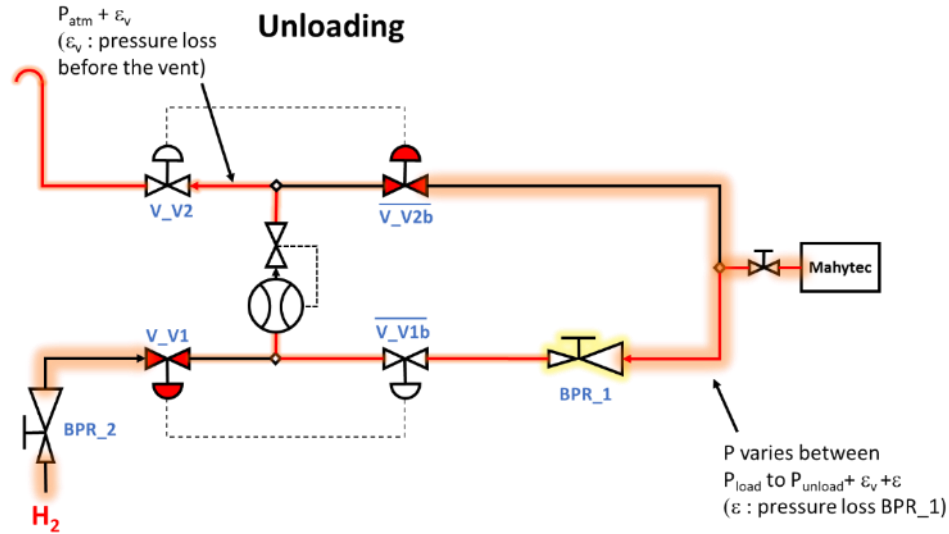
Backward pressure regulator
Upward Pressure Regulator
Valve
Needle Valve

Loading



Mass flow works at P_{source}

Unloading



Mass flow works at $\sim P_{\text{atm}}$

+ same kind of correction that with needle valves (but no "pshit" effect)

- Measuring capacity with thermal mass flowmeters seems to be the best solution

But it is still delicate since a large range of flow rate and pressure are involved

- Thermal mass flowmeter, even though frequently used for measuring tank capacity, are not so accurate:

A precision <2% could be attained taking a few precautions

- Some uncertainty origins have been detected / enlighten :

- ✓ Some are understood and can be corrected by improving the test bench design

Test bench geometries have been proposed, but it is necessary to test them

- ✓ Some are not understood and necessitate more investigations

Mass flow deviation at low pressures (Brooks)

Understand why / Test others (Bronkhorst)