Chemical Compatibility and Wettability of various Materials with various Working Fluids Two-Phase and Heat Pump Systems

Colin Butler, Jeff Punch

colin.butler@ul.ie

UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

STOKES LABORATORIES FLUID DYNAMICS

Final Review
ESA ESTEC, Noordwijk, Netherlands

20 June 2023

ESA Contract No. 4000131448/20/NL/RA

Introduction

- **Contractor:** University of Limerick (UL), Limerick, IE.
- Faculty of Science and Engineering \ Bernal Institute \ Stokes Labs
- Research topics and experience:
  - Heat & Mass transfer, thermofluids (telecommunications, aerospace thermal management)
  - Materials (reliability, surface science, aerospace composites, bio-materials)
- Key people:

Dr. Colin Butler
Project Manager,
Main technical researcher

Prof. Jeff Punch
Technical support

Dr. Eric Dalton
Technical support

Introduction

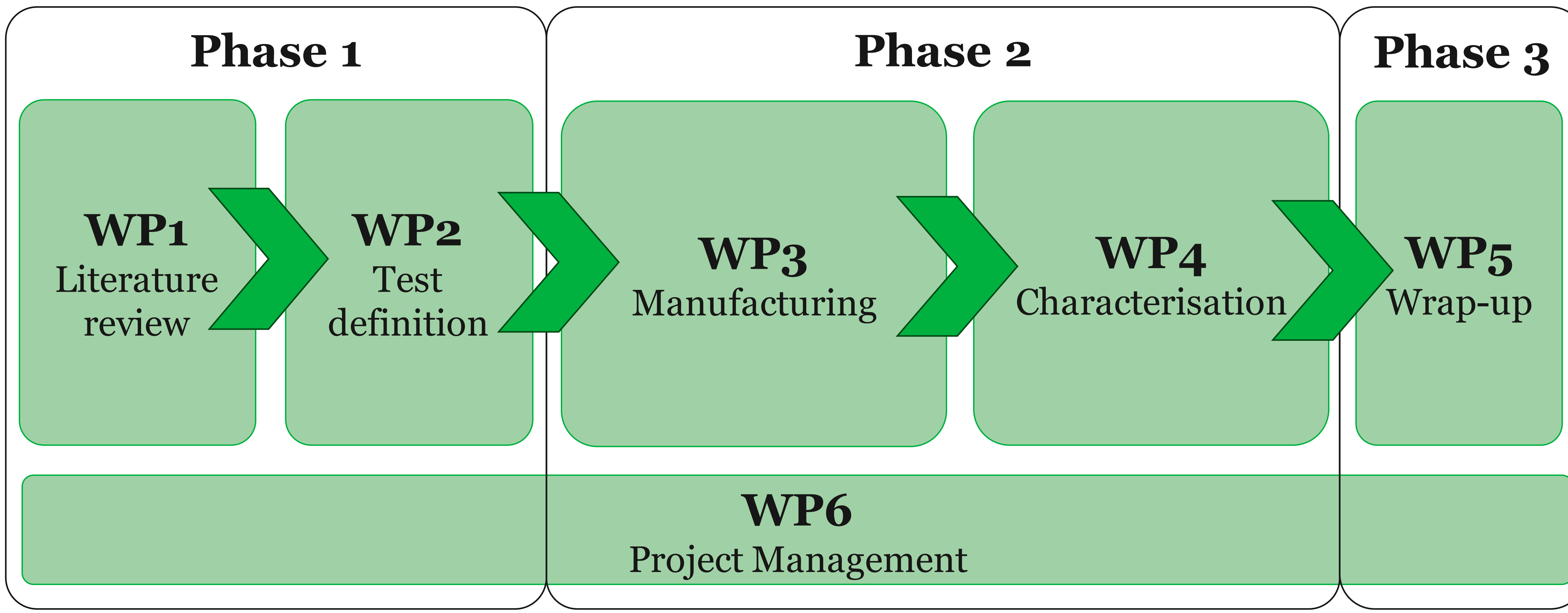
- **Project Motivation**
  - Generation of **Non-Condensable Gases (NCG)** can severally affect the performance of two-phase equipment.
  - **Materials compatibility testing** is required for all new equipment or materials to ensure NCG generation over expected lifetime is minimised.
  - A particular focus of this project is on **Additive Layer Manufacturing (ALM)** of Metals which allow for highly customisable and lightweight components.

- **Project Aims**
  - Investigate the **chemical compatibility** of different working fluids with:
    - Conventional/standard materials
    - ALM materials
    - Bi-metallic junctions

    applicable to two-phase systems.
  - Investigate the **wettability** of ALM materials with working fluids.
  - **Disseminate** the results.

UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

Introduction



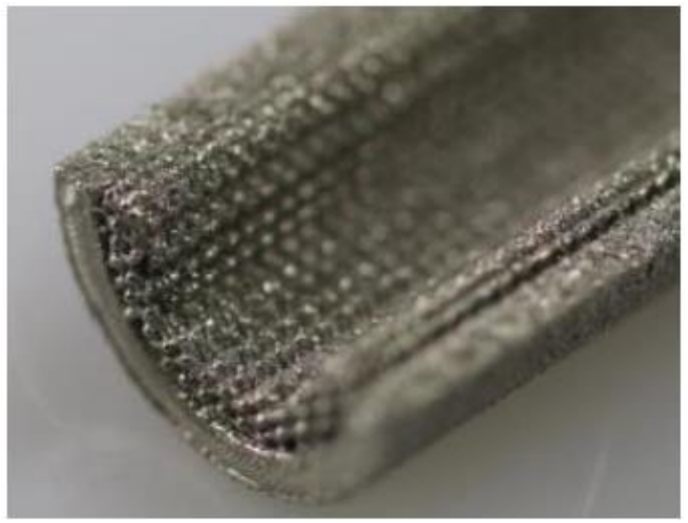
- **Project Duration**
  - September 2020 – June 2023 (2 year, 9 months)

UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

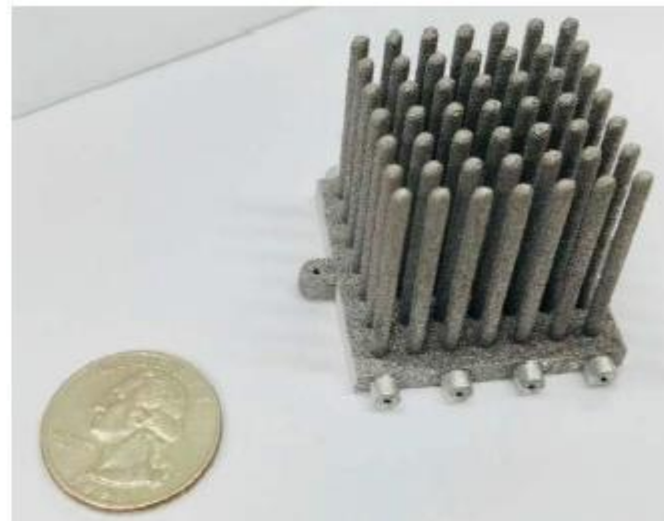
Contents

- **WP1 Literature review:** Identification of state-of-the-art and promising fluid-metal combinations.
- **WP2 Test definition:** Test requirements and test plan development.
- **WP3 Manufacture:** Sample and test rig manufacture.
- **WP4 Characterisation:** NCG long-term testing, corrosion analysis and wettability.
- **WP5 Wrap-up:** Conclusions and recommendations.

WP1 Literature review

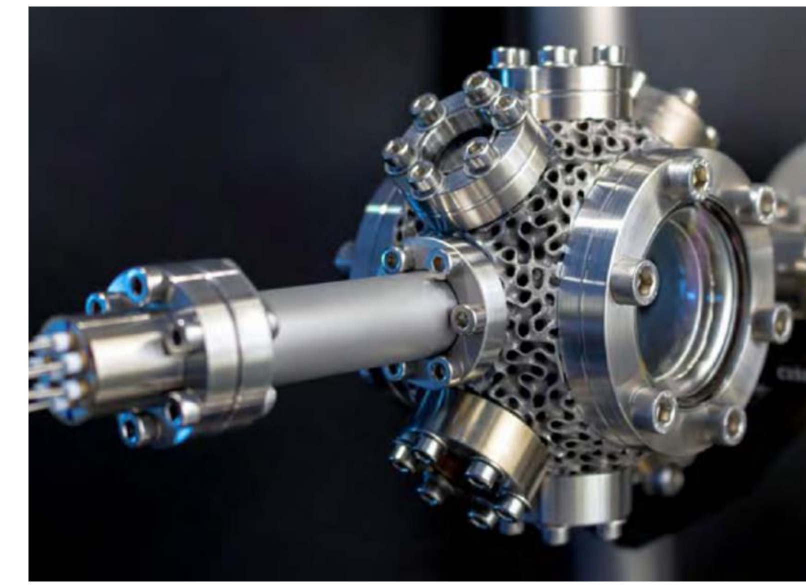


ALM titanium heat pipe section with integrated wick [McGlen & Sutcliffe, 2020]

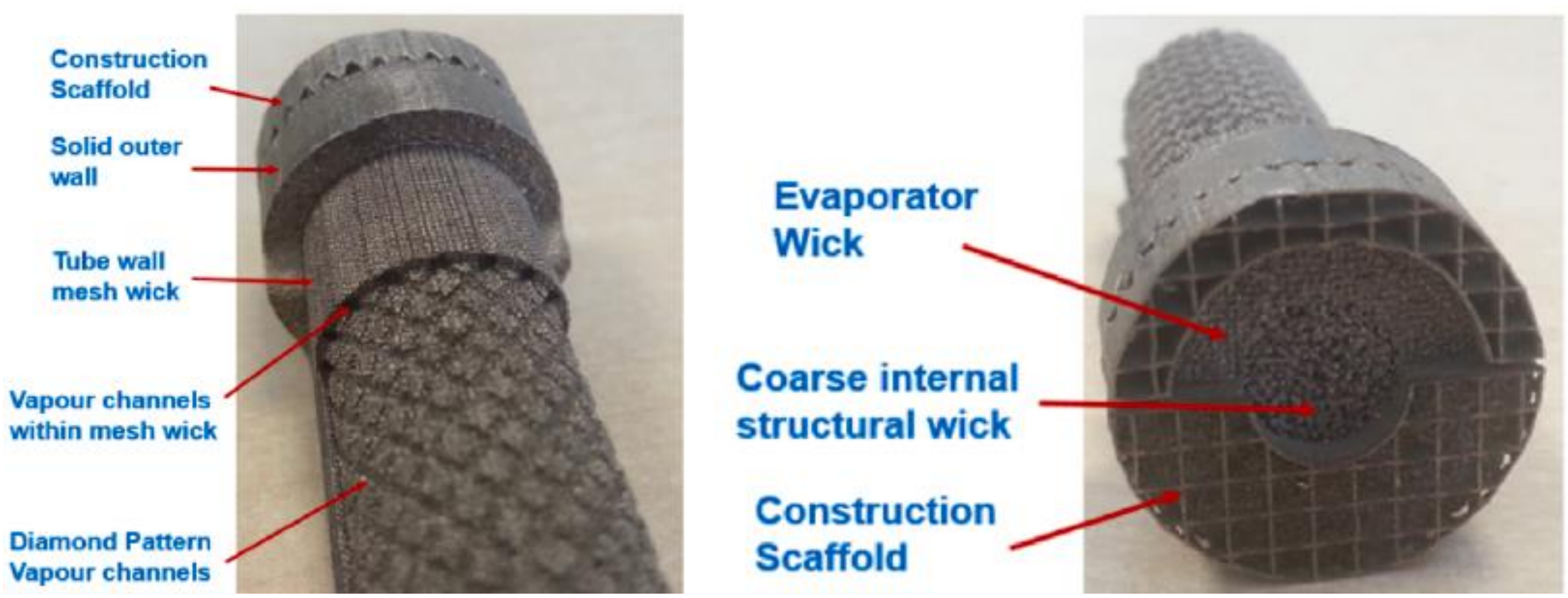


AlSi10Mg heat sink with integrated heat pipes and vapor chamber [Sunada & Rodriguez, 2018]

2-phase mechanically pumped fluid loop with ALM AlSi10Mg components [van Gerner, et al. 2019]



AlSi10Mg portable ultra-high vacuum chamber [Cooper, et al. 2021]



ALM titanium LHP evaporator demonstrator [McGlen, 2021]

ALM aluminium deployable radiator with OHP [Kuo, 2022]

WP1 Literature review

- **Water** for copper heat pipes in CubeSats.
- **Water or Toluene** for High Temperature applications.
- **Synthetic or natural refrigerants** for heat pumps (R-134a, R-1234ze, R-601a, R-744).
- **Bimetallic systems** in LHP evaporators, or pumped loop transfer lines.

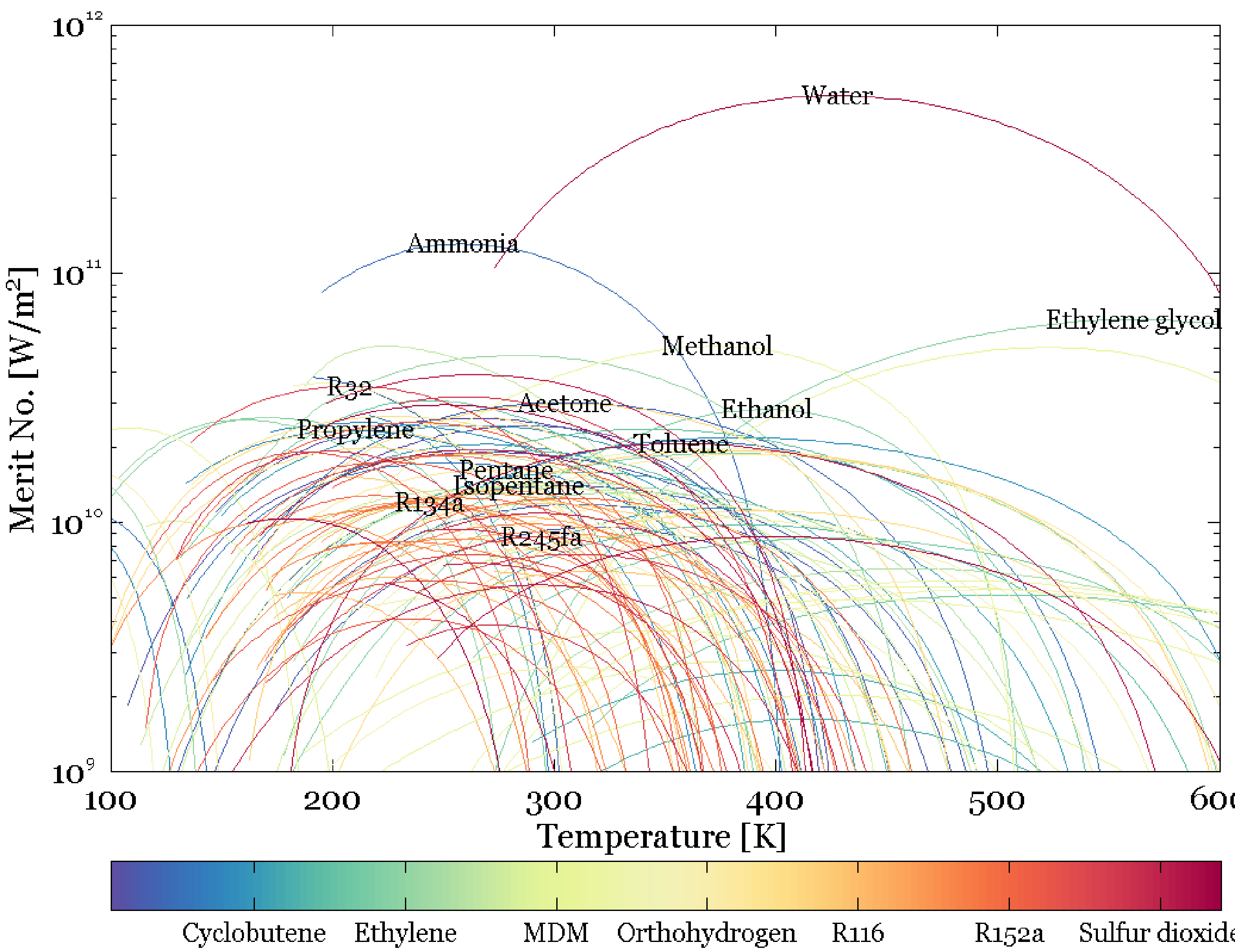
WP1 Literature review

- **Merit Number analysis**
  - Estimate the heat transfer performance of the large range of available working fluids, especially in useful temperature ranges that overlap.
  - Other factors need to be taken into account such as cost, availability, safety, etc.
  - NIST RefProp v10.0 with thermodynamic properties for 147 different working fluids.
  - **Heat Pipe:**

$$M = \frac{\rho_l h_{lv} \sigma}{\mu_l}$$

where

- ρ_l is the liquid phase density
- h_{lv} is the latent heat of vaporisation
- σ is the interfacial surface tension
- μ_l is the liquid phase dynamic viscosity



WP1 Literature review

- **Merit Number analysis**
  - **Loop Heat Pipe**
  - Because of the changing operating characteristics and geometries of LHPs, different figures of merit have been derived in literature.
  - For example:

$$M = \frac{\rho_v {h_{lv}}^{1.75} \sigma}{{\mu_v}^{0.25}}$$ *(Assuming that the largest pressure loss is caused by vapour loss in long thin transfer lines)*

$$\frac{4\sigma \cos\theta}{d_p} = f_{tur} \frac{\rho_v u_v^2}{2d_v} L_{LHP} + \frac{16 u_w \mu_l}{d_p^2}(d_2 - d_1) + \frac{32 u_l \mu_l}{d_l^2} L_{LHP}$$ *(Takes LHP geometry into account)*

  - Using LHP speciation from literature *[Mishkinis, et al., 2003]*.

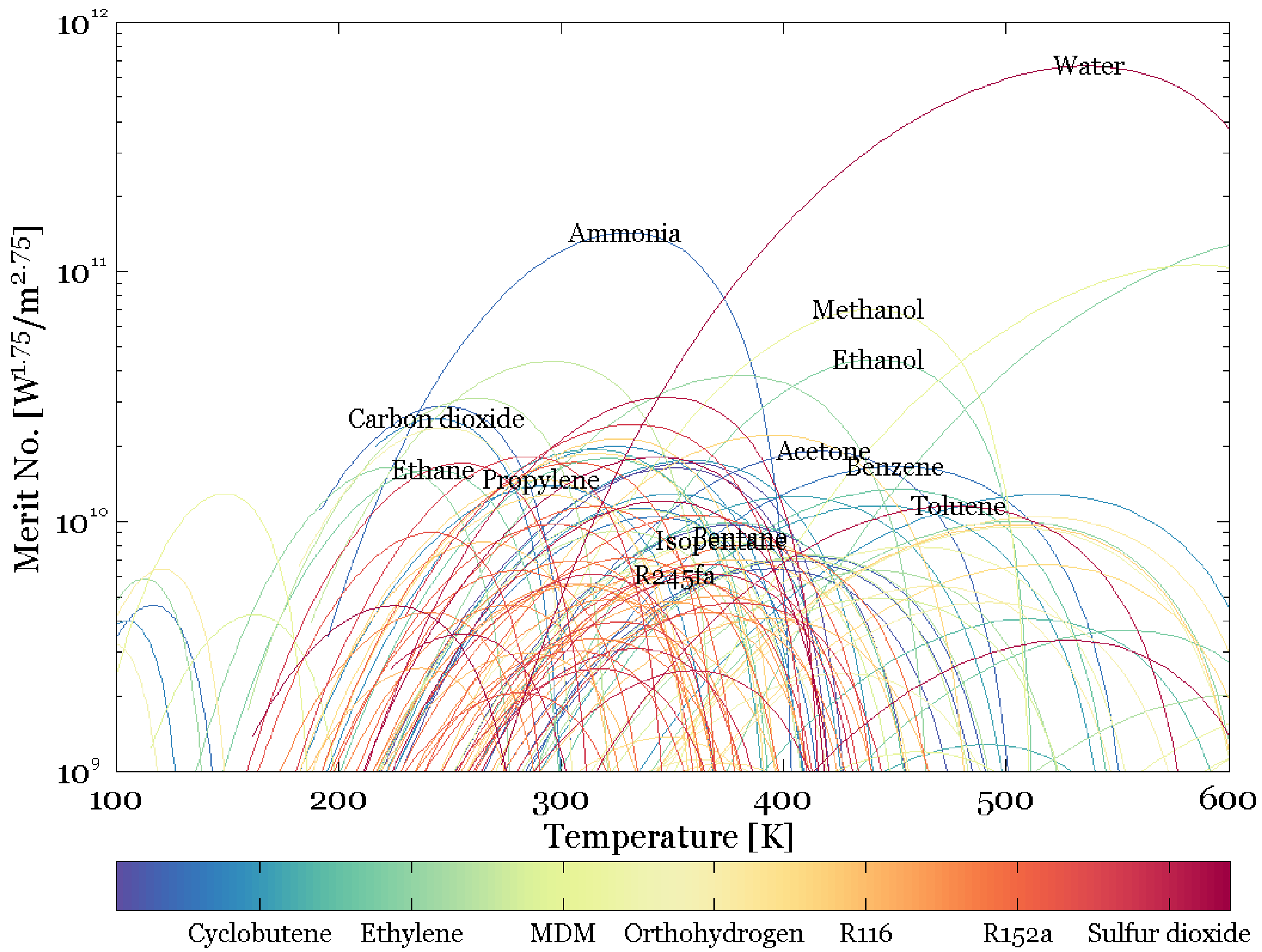
UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

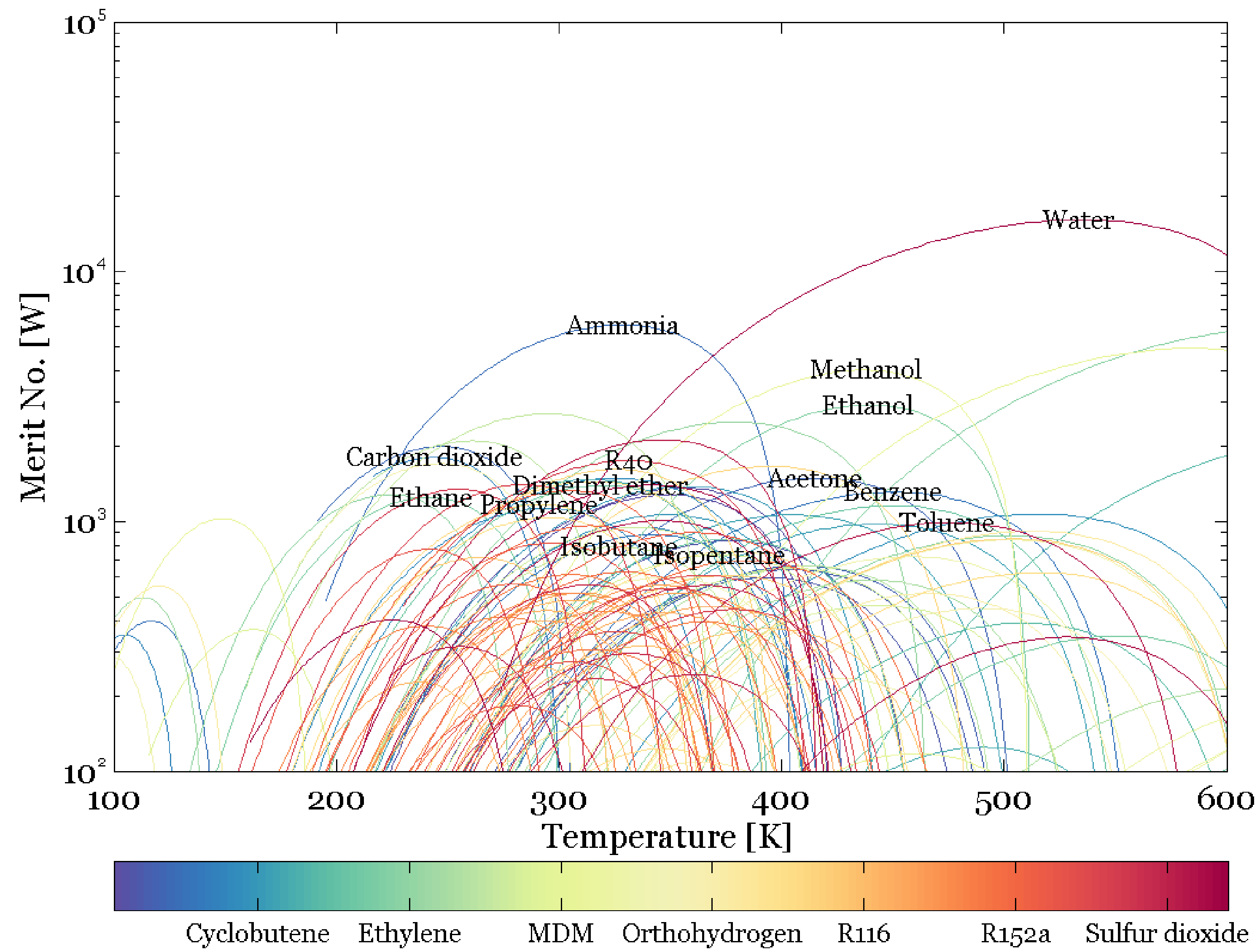
WP1 Literature review

- **Merit Number analysis**
  - **Loop Heat Pipe**

$$M = \frac{\rho_v {h_{lv}}^{1.75} \sigma}{{\mu_v}^{0.25}}$$

$$\frac{4\sigma \cos\theta}{d_p} = f_{tur} \frac{\rho_v u_v^2}{2 d_v} L_{LHP} + \frac{16 u_w \mu_l}{d_p^2}(d_2 - d_1) + \frac{32 u_l \mu_l}{d_l^2} L_{LHP}$$

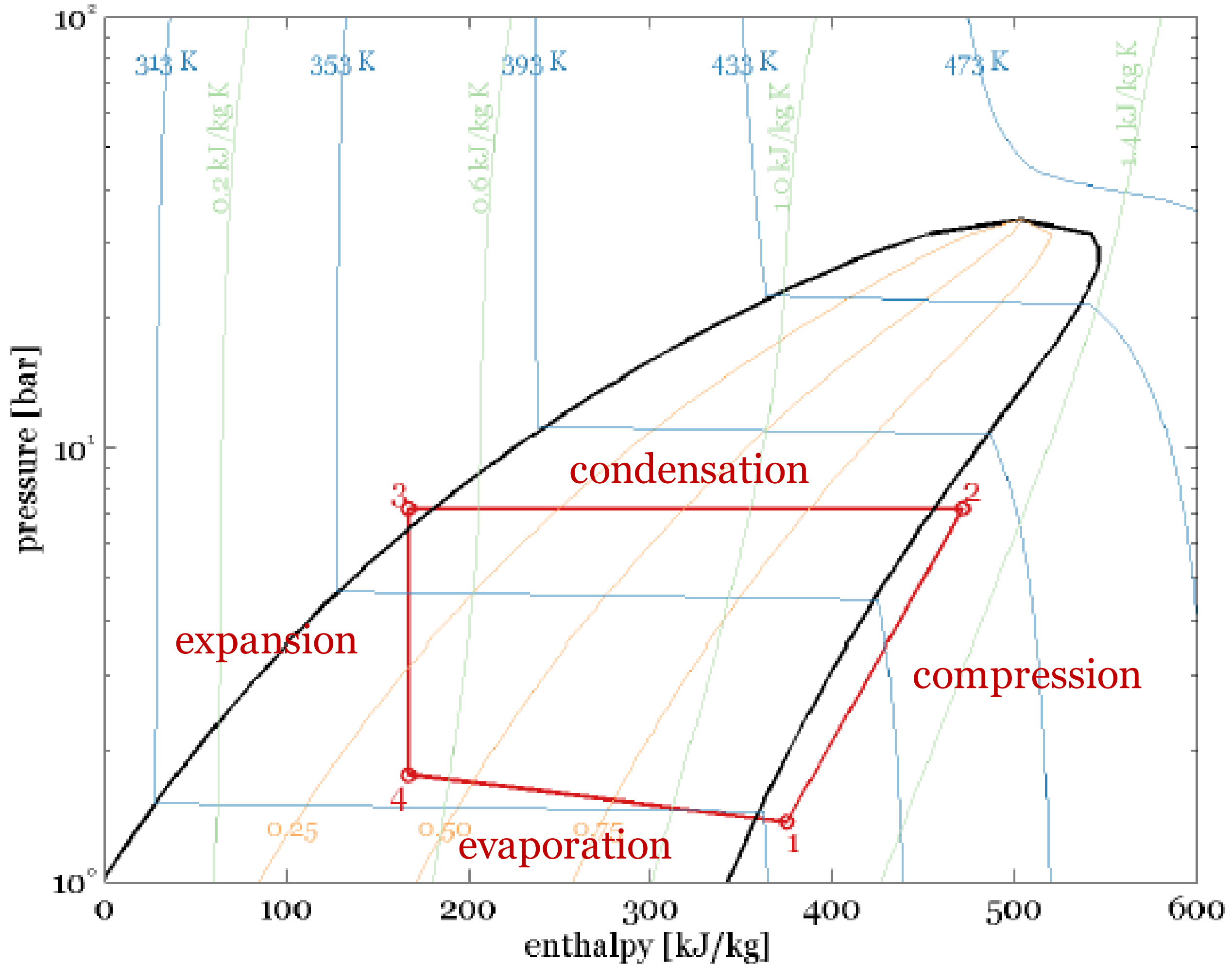




WP1 Literature review

- **Merit Number analysis**
  - **Heat Pump**
  - For heat pump using vapour compression cycle, Coefficient of Performance is the cooling capacity of the heat pump, divided by the compressor power:

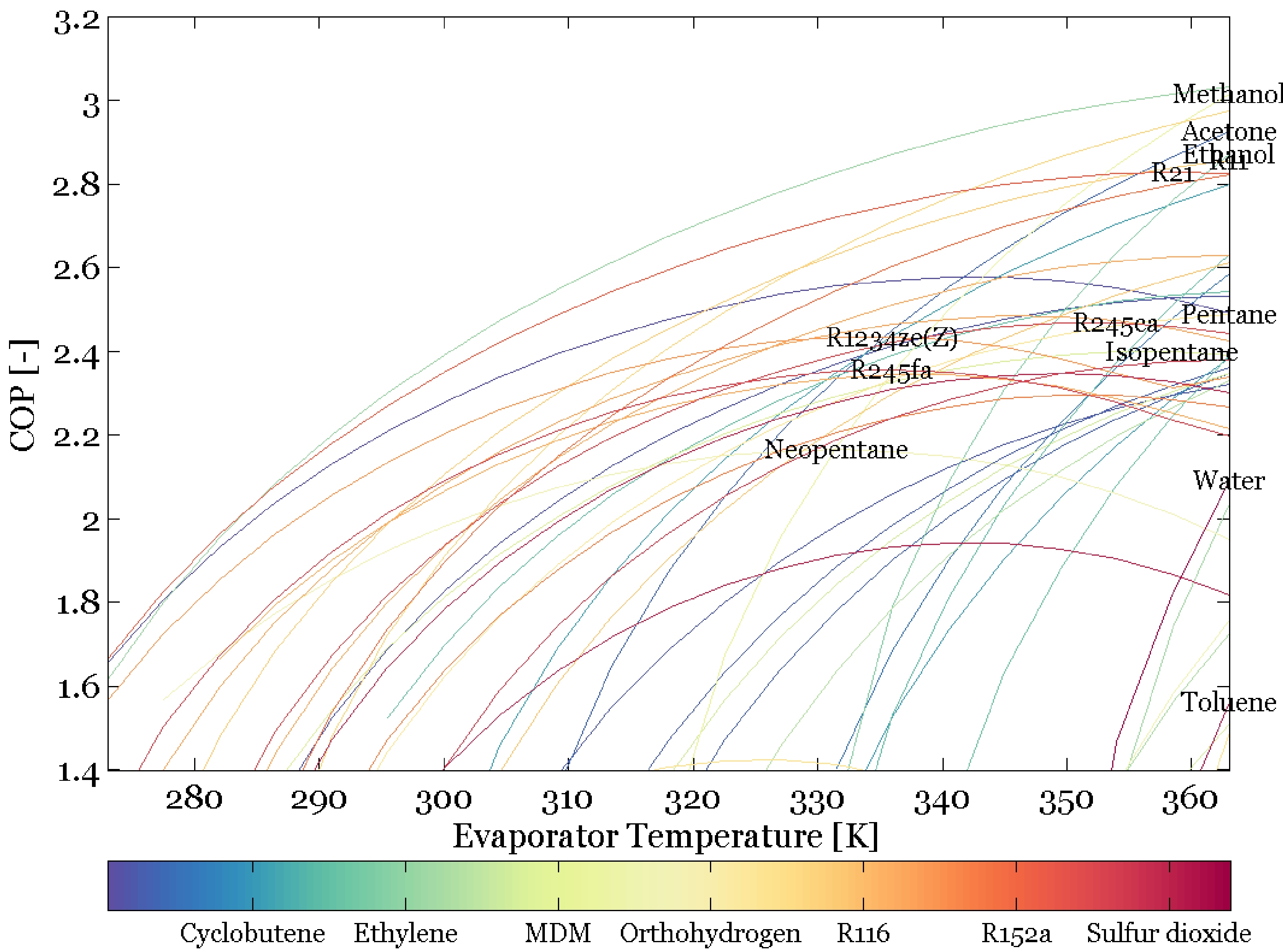
$$COP = \frac{P}{W_{compressor}} = \frac{h_1 - h_4}{h_2 - h_1}$$



  - Using spacecraft heat pump speciation from literature *[van Gerner, et al., 2014]*.

WP1 Literature review

- **Merit Number analysis**
  - **Heat Pump**



WP1 Literature review

- **Metals**

Name	**Advantages**	**Disadvantages**
Copper	Excellent *k*, Compatible with most fluids	Incompatible with NH_3, ALM not widely available, High ρ
Aluminium	Very good *k*, Low ρ, ALM	Incompatible with water
Titanium	Low ρ, ALM, Compatible with most fluids	Expensive, Poor *k*
Stainless steel	ALM, Compatible with most fluids	High ρ, Poor *k*
Nickel	Good *k*	Unknown compatibility for many fluids
Invar	Good *k*, ALM, Excellent CTE	High ρ Unknown compatibility

WP1 Literature review

- **Selection**

Fluid	Properties									H&S	Metal Combinations & Compatibility							
											Standard					ALM		
	Triple Point Temperature, T_t [K]	Critical Temperature, T_c [K]	Melting Point Temperature at 1 atm [K]	Boiling Point Temperature at 1 atm [K]	Vapour Pressure at 293 K [bar]	Useful Working Temperature range [K]	HP Merit No. at $(T_t+T_c)/2$ [GW/m2]	ODP [-]	GWP [-]	ASHRAE Safety Group	Aluminium	Copper	Stainless steel	Titanium	Nickel	AlSi10Mg	SS316L	Ti6Al4V
Acetone	178.50	508.10	176.60	329.22	0.24	223-373	28.3				G(HL)	F(O) G(HOL)	G(HL)		G(L)	G(HP)		
Ammonia (R-717)	195.49	405.56	195.50	239.83	8.53	208-373	110.3	0	0	B2L	F(HO) G(H)		F(L) G(HL)	G(L)	F(L) G(L)	G(L)	G(L)	G(H)
Carbon dioxide	216.59	304.13	216.59	194.69	57.09		14.6	0	1	A1					G(P) F(P)			
Ethane	90.37	305.32	90.38	184.57	37.53	103-273	24.5	0	5.5	A3		G(O)	G(L)					
Ethanol	159.00	514.71	159.05	351.57	0.06	273-403	22.6				G(L)	G(OL)	G(L)		G(L)			
Ethylene glycol	260.60	719.00	260.15	470.31	7×10^{-5}		56.7					G(O)						
Isobutane (R-600a)	113.73	407.81	113.77	261.40	3.01		13.5	0	3	A3	G(H)	G(P)						
Isopentane (R-601a)	112.65	460.35	112.66	300.98	0.76		14.1	0	4	A3	G(P)							
Methanol	175.61	512.60	175.63	337.63	0.13	213-398	48.9					G(O)	G(HL)		G(L)	G(H)		
Nitrogen	63.15	126.19	63.17	77.35		70-113	7.1	0	0	A1		G(HL)	G(L)		G(L)			
Oxygen	54.36	154.58	54.37	90.19		73-119	14.7	0	0									
Pentane (R-601)	143.47	309.21	143.48	309.21	0.56	173-393	15.6	0	4	A3	G(H)	G(HL)	G(L)					
Perfluorohexane (FC-72)	187.07	448.00	186.05	330.27	0.23			0	9300		F(O) G(O)					G(L)		
Propylene (R-1270)	87.95	364.21	88.59	225.53	10.13	123-313	23.2	0	1.8	A3			F(L) G(L)		G(L)			
R-1234ze	238.00	423.27		282.88	1.48		10.5	0	6	A2L		G(H)						
R-134a	169.85	374.21	169.85	247.08	5.69	193-323	11	0	1300	A1	G(L)	G(HL)	F(O) G(OL)					
R-152a	154.56	386.41	154.55	249.13	5.11		17.8	0	138	A2		G(H)						
R-161	130.00	375.25	129.95	235.61	8.01		24.7	0	4	A2L								
R-245ca	196.00	447.57	191.15	298.41	0.82			0	716									
R-245fa	170.00	405.56	153.15	288.20	1.22		8.7	0	853	B1		G(HP)				G(P)		
R-32	136.34	351.26	136.35	221.50	14.68		31.6	0	677	A2L								
R-40	175.51	416.30	175.55	249.17	4.96		23.3	0.02	13	B2								
Toluene	178.00	419.21	178.25	383.75	0.03	223-553	20.1				G(H)		G(HL)					
Water	273.16	647.10	273.15	373.12	0.02	293-553	489.1	0	0.02	A1	G(OL)	F(H) G(HOL)	G(OL)	G(HL)	G(L)		G(H)	G(H)

University of Limerick Ollscoil Luimnigh | Bernal Institute

WP1 Literature review

- **Final selection**

Metal / Fluid	Conventional		ALM					Bimetallic	Other		
	Al6061	**SS316L**	**Ti6Al4V**	**AlSi10Mg**	**SS316L**	**AlSi7Mg**	**Invar**	**Al6061 /SS316L**	**SCouP with AlSi10Mg**	**SCouP with AlSi7Mg**	**SCouP with ALM SS316L**
Ammonia	x	x	x	x	x	x	x	x	x	x	x
Acetone			x	x	x	x					
Ethylene glycol	x	x		x	x	x					
Methanol			x		x		x				
Propylene				x	x	x					
Toluene			x	x	x	x	x	x			
Water			x		x						

- Total no. of combinations = 34.
- Applicable to both space and earth-based systems.

UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH Bernal Institute

WP1 Literature review

- **Final selection**

Metal / Fluid	Conventional		ALM					Bimetallic	Other		
	Al6061	SS316L	Ti6Al4V	AlSi10Mg	SS316L	AlSi7Mg	Invar	Al6061 /SS316L	SCouP with AlSi10Mg	SCouP with AlSi7Mg	SCouP with ALM SS316L
Ammonia	x	x	x	x	x	x	x	x	x	x	
Acetone			x	x	x	x					
Ethylene glycol	x	x		x	x	x					
Methanol			x		x						
Propylene				x	x	x					
Toluene			x	x	x	x					
Water			x		x						

Spur Industries, Inc. roll bonded 3003 Al – 304L SS bi-metallic junction.

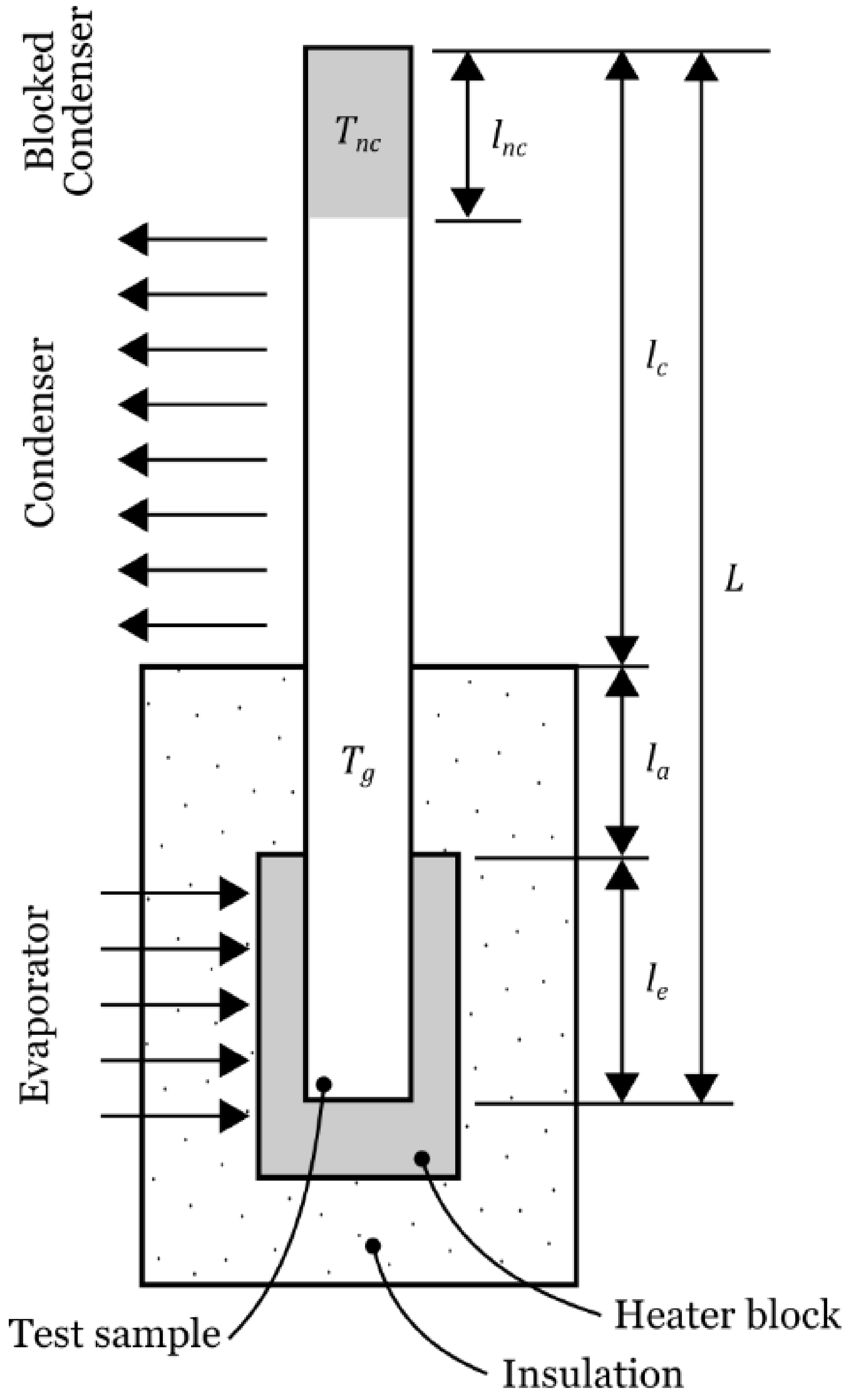
SCouP srl Shape Memory Alloy coupling

- Total no. of combinations = 34.
- Applicable to both space and earth-based systems.

WP2 Test definition

- From **ECSS-E-ST-31-02C**, standard method for life-testing of 2-phase devices is the **Gas Plug Test**.

- Device setup in reflux mode.
- Isothermal temperature at the evaporator.
- Temperature profile along the sample monitored over extended period of time.
- NCG builds up in the top of the condenser.



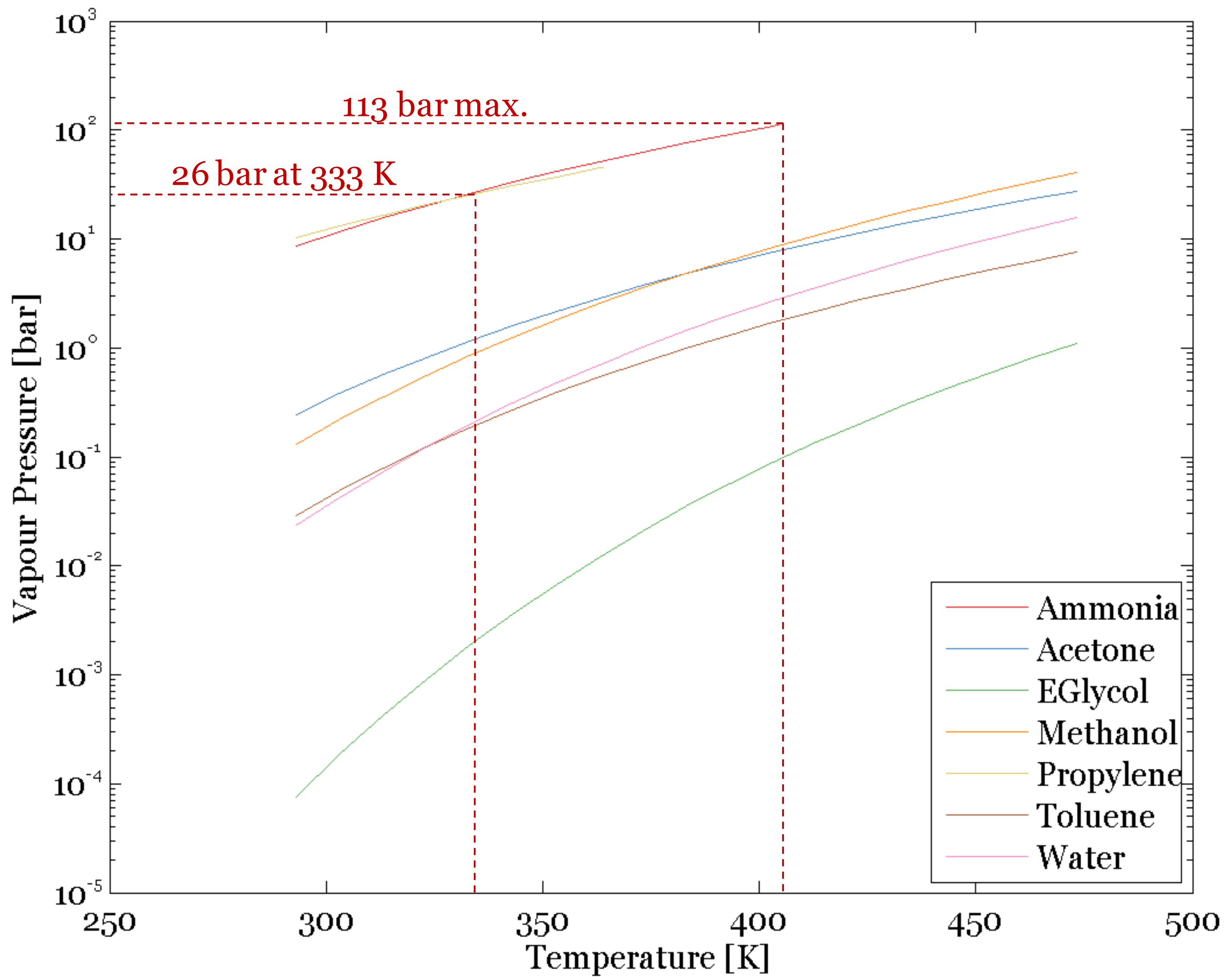
WP2 Test definition

- **Sample Design**
  - Thermosyphon devices.
  - 12.7 mm (½ inch) outside diameter (*d*).
  - 180 – 400 mm long depending on material thermal conductivity.
  - Wall thickness (*t*) determined from calculation of hoop stress for a cylindrical pressure vessel:

$$\sigma_\theta = \frac{P_v d}{2t}$$

  - A value of 0.9 mm wall thickness gives a minimum factor of safety of 7 for aluminium samples during testing.
  - 0.9 mm ~ BWG 20 gauge standard tubing (0.887 mm).
  - ALM feature size tolerance of +/- 0.15 mm.

  - **3** identical samples for each fluid metal combination.



UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH Bernal Institute

WP2 Test definition

- **Conventional supplier selection**

Supplier \ Material	SS316L	Al6061	Ti CP Grade 2
Swagelok, IE	X		
TW Metals, UK		X	
Goodfellow, DE	X	X	X

- **ALM supplier selection**

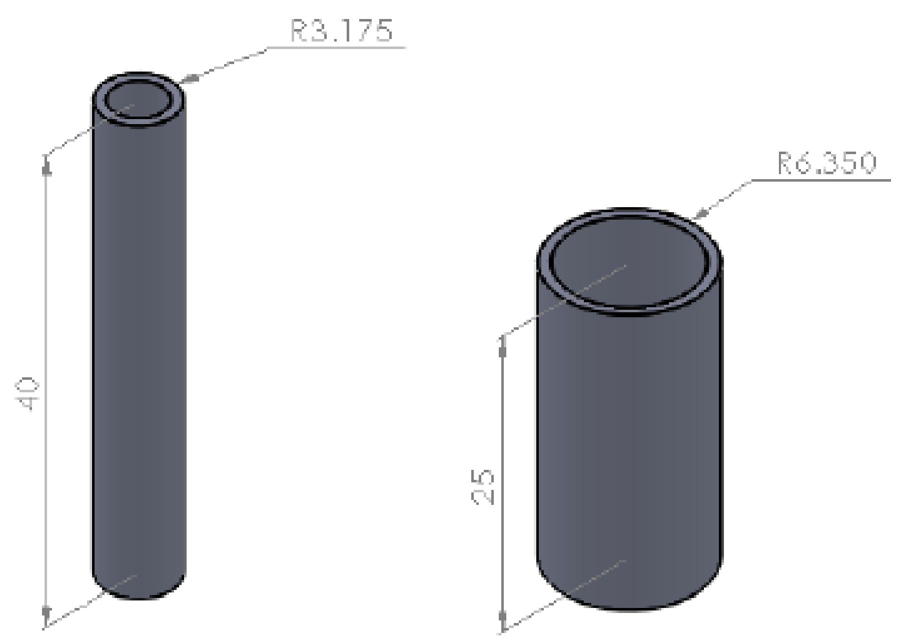
Supplier \ Material	SS316L	Ti6Al4V	AlSi10Mg	AlSi7Mg	Invar
Croom Precision Medical, IE	X	X	X		
Polyshape, FR				X	
Sirris, BE					X

- Selections based on material availability, pricing, and lead time.

UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH Bernal Institute

WP2 Test definition

- **ALM coupon testing**
  - Before manufacture of thermosyphon devices, samples of each material from selected supplier was acquired and tested (*except Invar*).
  - Two geometries representation of:
    - Main thermosyphon tube
    - Filling tube



(dimensions in mm)

AlSi10Mg ALM build plate

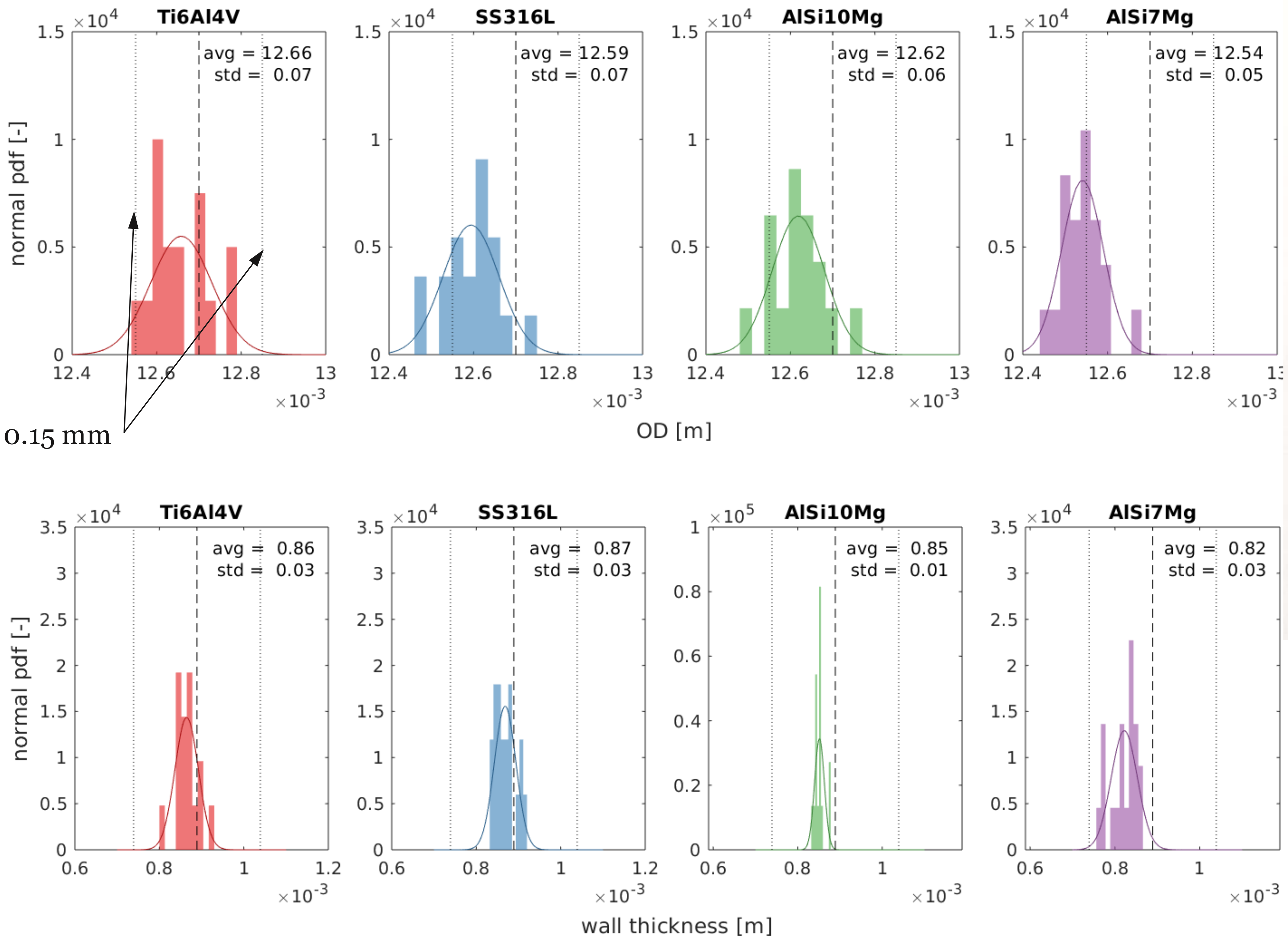
WP2 Test definition

- **ALM coupon testing**
  - **Micrometry** with optical microscope and image processing

Outside Diameter

Wall Thickness

ALM tolerance +/- 0.15 mm



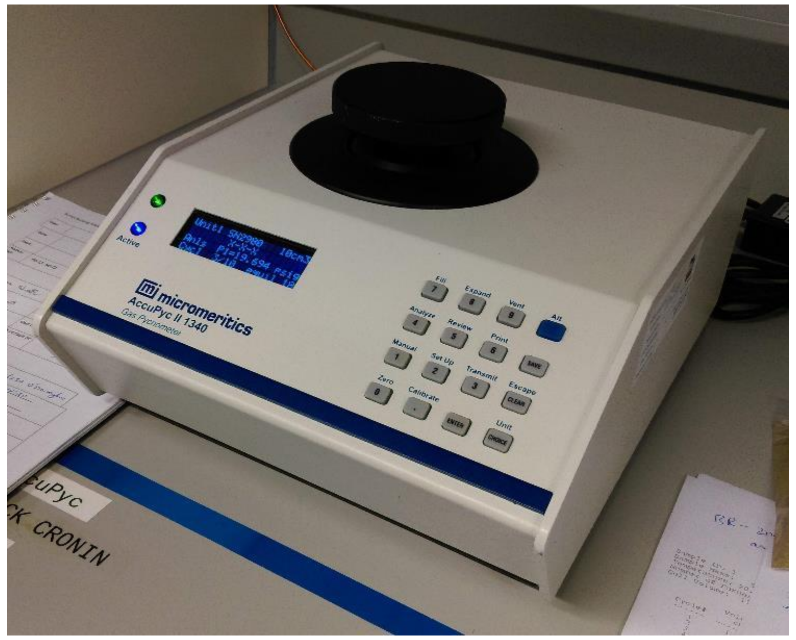
ALM test pieces (12.7 mm OD, 0.9 mm wall, 25 mm long)

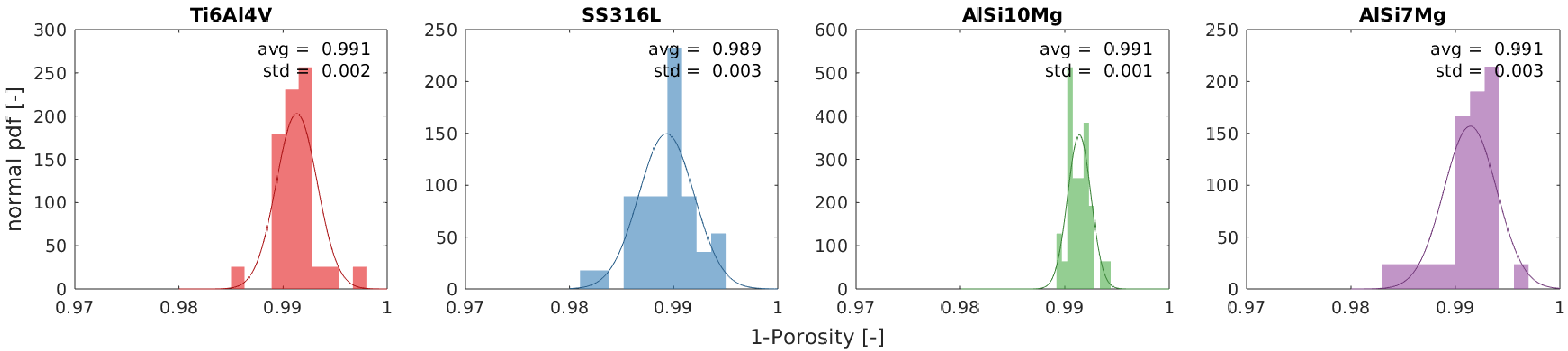
WP2 Test definition

- **ALM coupon testing**
  - **Porosity** (Micromeritics AccuPyc II 1340 Pycnometer)
  - Gas (He) displacement method using Boyle's Law
  - Density measurement:

$$1 - Porosity = \frac{m_{meas}/V_{meas}}{\rho_{ref}}$$

  - ρ_{ref} from material datasheet





UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH Bernal Institute

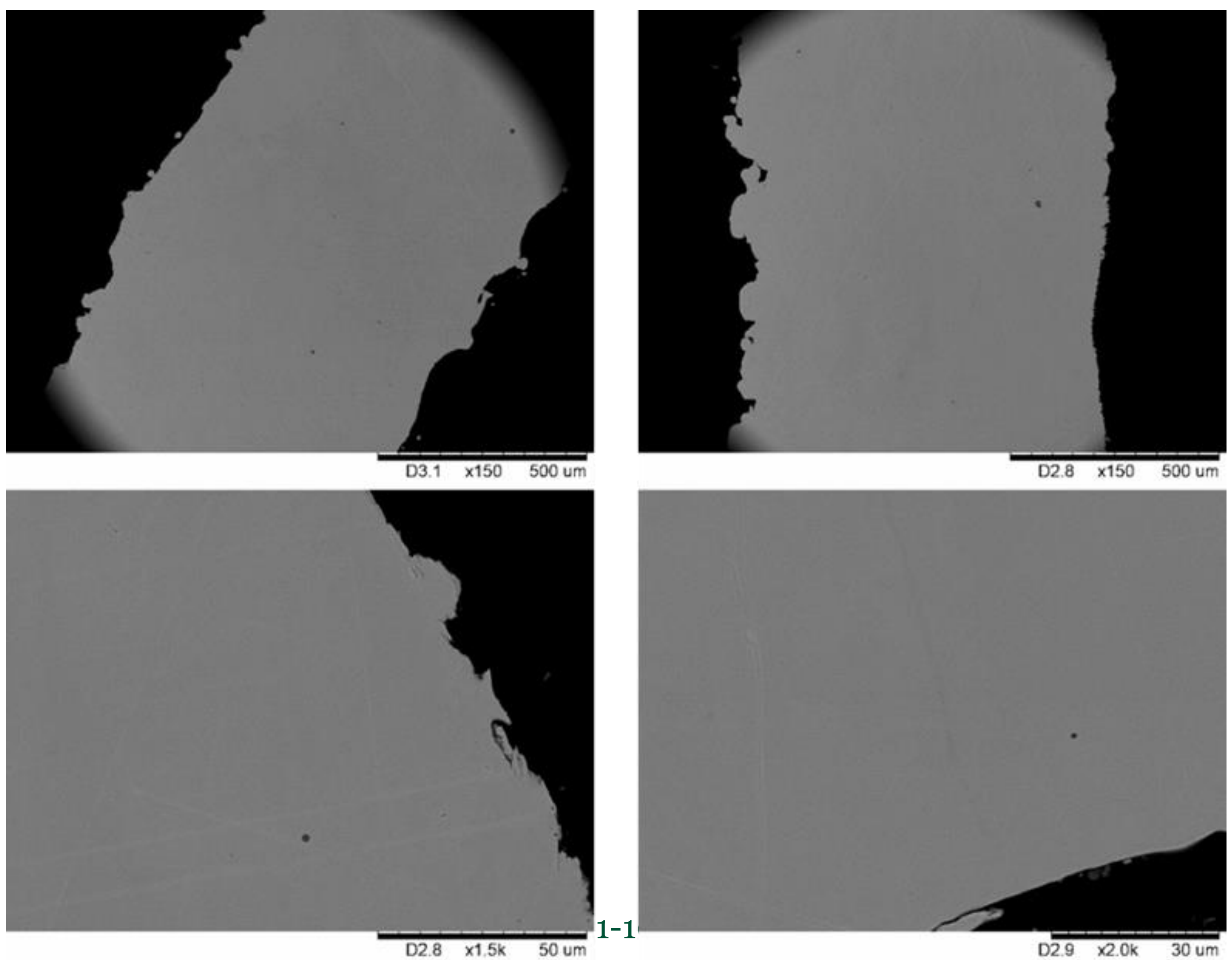
WP2 Test definition

- **ALM coupon testing**
  - **Porosity**
  - SEM and EDX: **SS316L**

radial | **longitudinal**

x 150 (1.1 µm/px)

x 2.0k (0.08 µm/px)



Element	C [% wt] from EDX	C [% wt] from spec. sheet
Fe	57.53 ± 2.0	62 – 69
Cr	14.01 ± 0.5	16 – 18
Ni	10.37 ± 0.5	10 – 14

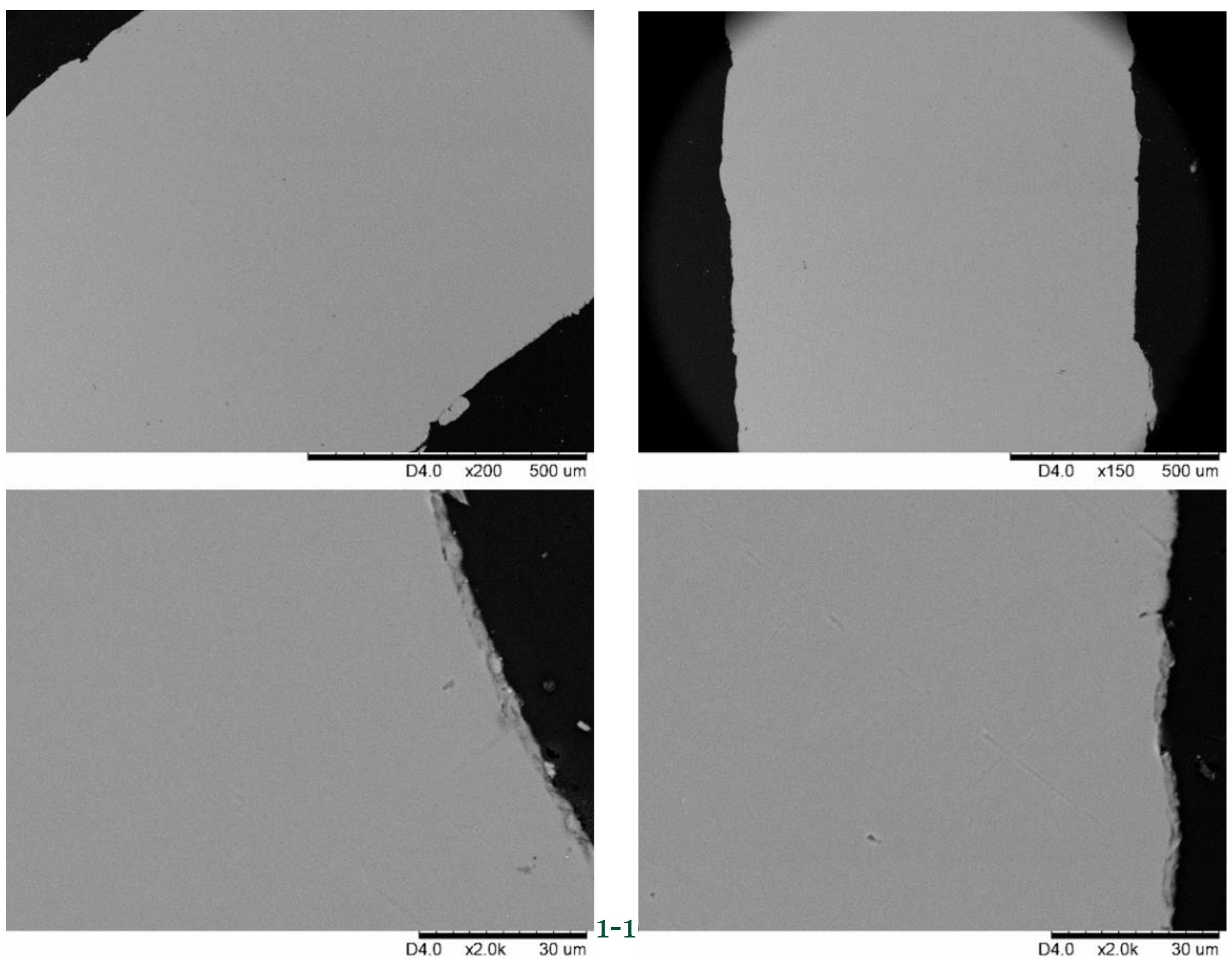
WP2 Test definition

- **ALM coupon testing**
  - **Porosity**
  - SEM and EDX: **AlSi10Mg**

radial | **longitudinal**

x 150 (1.1 µm/px)

x 2.0k (0.08 µm/px)



Element	C [% wt] from EDX	C [% wt] from spec. sheet
Al	89.14 ± 5.4	88 – 91
Si	9.62 ± 0.59	9 – 11
Mg	1.24 ± 0.13	0.25 – 0.45

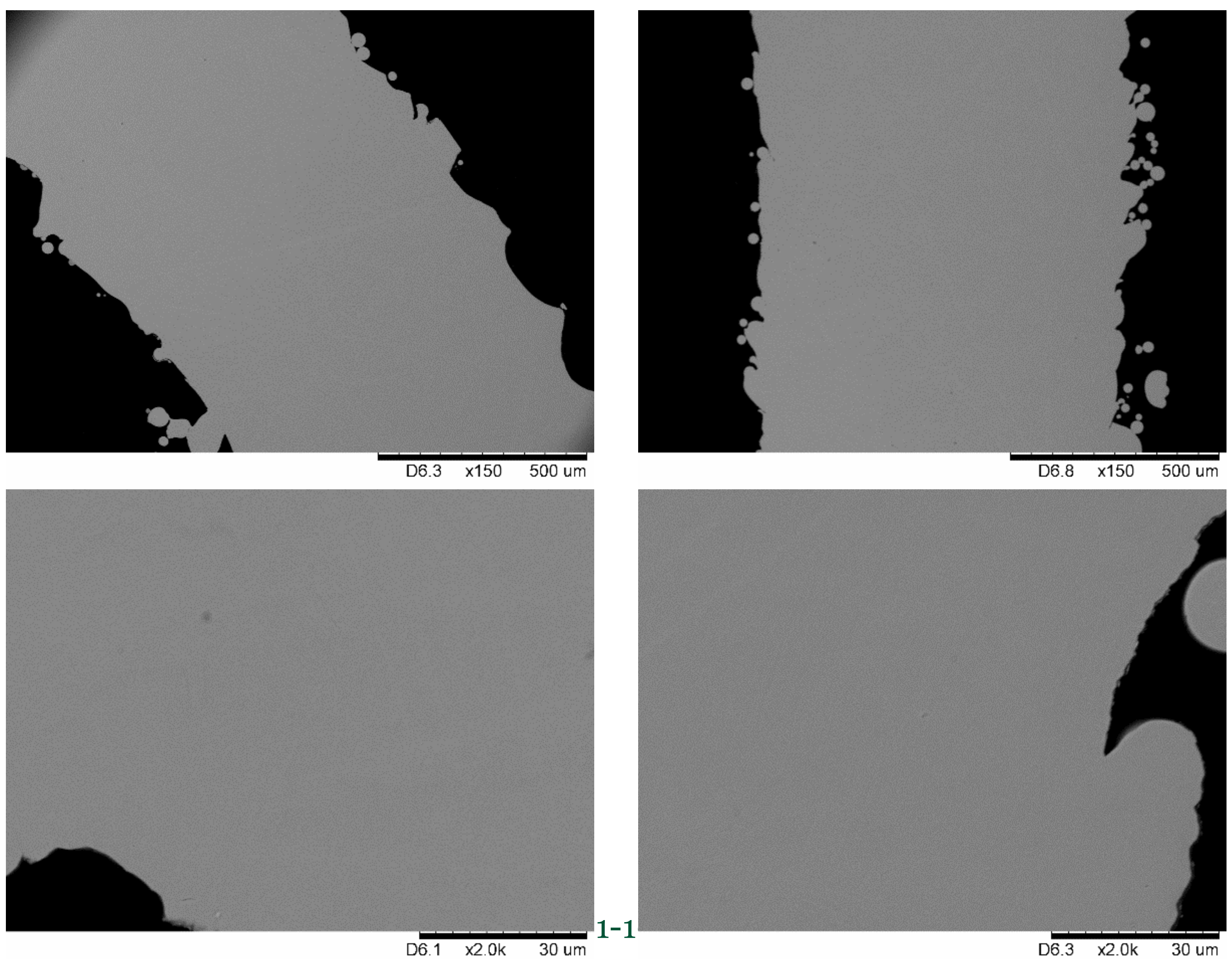
WP2 Test definition

- **ALM coupon testing**
  - **Porosity**
  - SEM and EDX: **Ti6Al4V**

radial **longitudinal**

x 150 (1.1 µm/px)

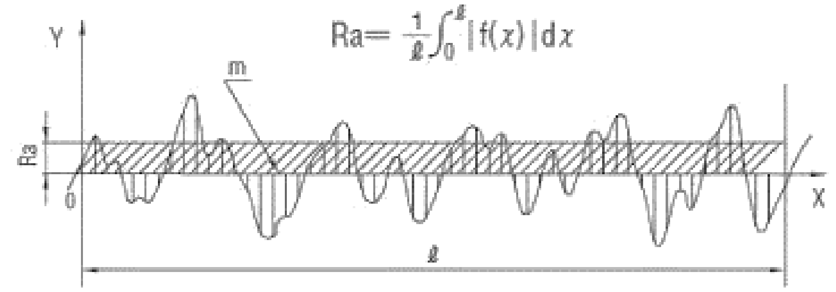
x 2.0k (0.08 µm/px)



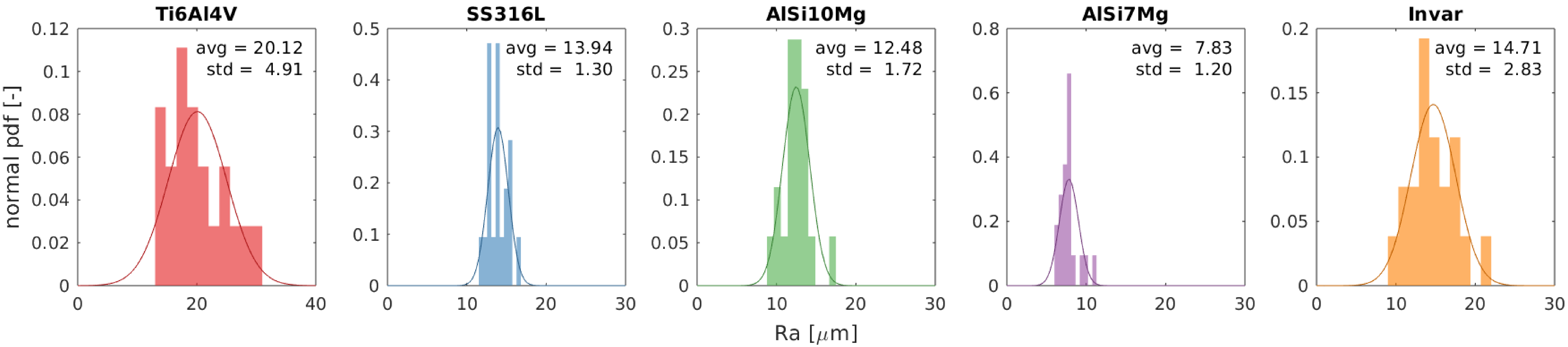
Element	C [% wt] from EDX	C [% wt] from spec. sheet
Ti	88.93 ± 3.1	89 – 91
Al	6.24 ± 0.3	5.5 – 6.5
V	2.18 ± 1.3	3.5 – 4.5

WP2 Test definition

- **ALM coupon testing**
  - **Surface Roughness** (Mitutoyo Surftest SJ-210 profilometer)
  - Measurements performed on OD in axial direction
  - **Ra** is defined as "*the mean of the absolute values of the evaluation profile deviations from the mean line*"

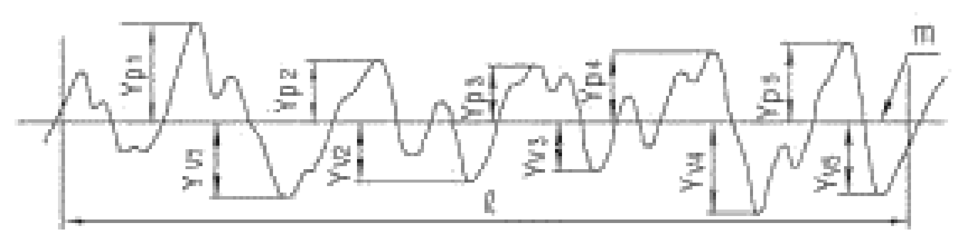


Process	Ra (μm)
Electropolished	0.25
Cold rolling	0.8 – 1.6
Boring or Turning	0.4 – 6.3
Sand-blasting	12.5 – 25

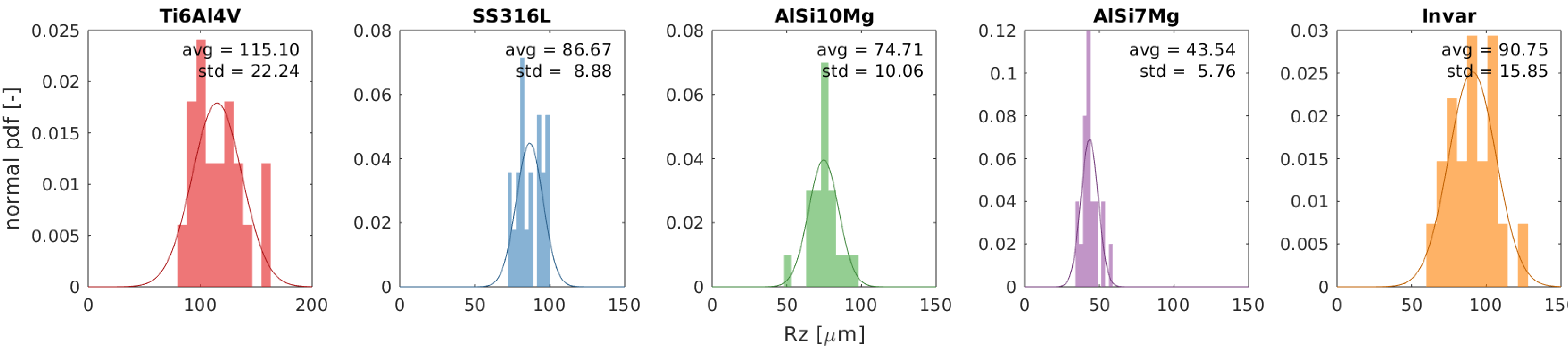


WP2 Test definition

- **ALM coupon testing**
  - **Surface Roughness** (Mitutoyo Surftest SJ-210 profilometer)
  - Measurements performed on OD in axial direction
  - **Rz** is defined as "*the sum of largest peak and valley in the evaluation profile*"

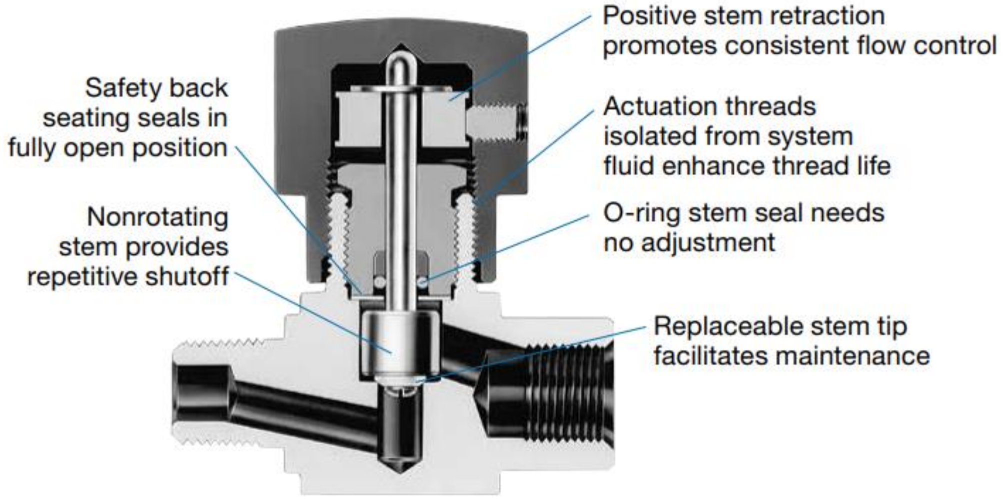


$$Rz = \frac{|Yp_1 + Yp_2 + Yp_3 + Yp_4 + Yp_5| + |Yv_1 + Yv_2 + Yv_3 + Yv_4 + Yv_5|}{5}$$



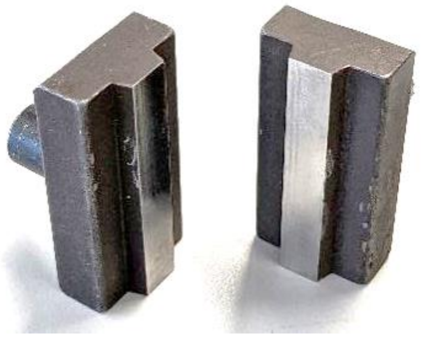
WP2 Test definition

- **ALM coupon testing**
  - **Crimping and sealing**
  - 3 identical samples for each fluid metal combination => 1 sample with valve + 2 crimp sealed.
  - Swagelok SS-14DKS4 sampling valve.



  - ALM material testing and crimping geometry and tool development.

G-22 Hydraulic crimping tool with hardened D2 tool steel inserts



6.35 mm jaws

Extended 6.35 mm jaws

12.7 mm jaws

WP2 Test definition

- **ALM coupon testing**
  - **Crimping and sealing**
  - As-built ALM filling tube samples:

Ti6Al4V

AlSi10Mg

SS316L

WP2 Test definition

- **ALM coupon testing**
  - **Crimping and sealing**
  - Heat treatments performed in Carbolite GHA 12/450 horizontal tube furnace in a vacuum environment.
  - In general, from literature, and previous work with AlSi10Mg, decrease in tensile strength but increase in ductility.

Ti6Al4V
850°C, 2 hr dwell

AlSi10Mg
300°C, 2 hr dwell

AlSi10Mg
400°C, 2 hr dwell

WP2 Test definition

- **ALM coupon testing**
  - **Crimping and sealing**
  - Continued development with standard material coupons (6.35 mm OD, 2.0 mm ID).
  - => Smaller ID produced better crimp, less tendency to crack.
  - Top section removed with bolt cutter.
  - Crimps were Helium leak tested (< 1 x 10^{-9} mbar.L/s) and proof pressure tested to 20 bar.

SS316L
(6.35 mm OD, 2.0 mm ID)
6.35 mm crimp

Al6082-T6
(6.35 mm OD, 2.0 mm ID)
12.7 mm crimp

Ti CP Grade 2
(6.35 mm OD, 4.55 ID)
12.7 + 6.35 mm crimp
Failed He leak test

WP2 Test definition

- **ALM coupon testing**
  - **Crimping and sealing**

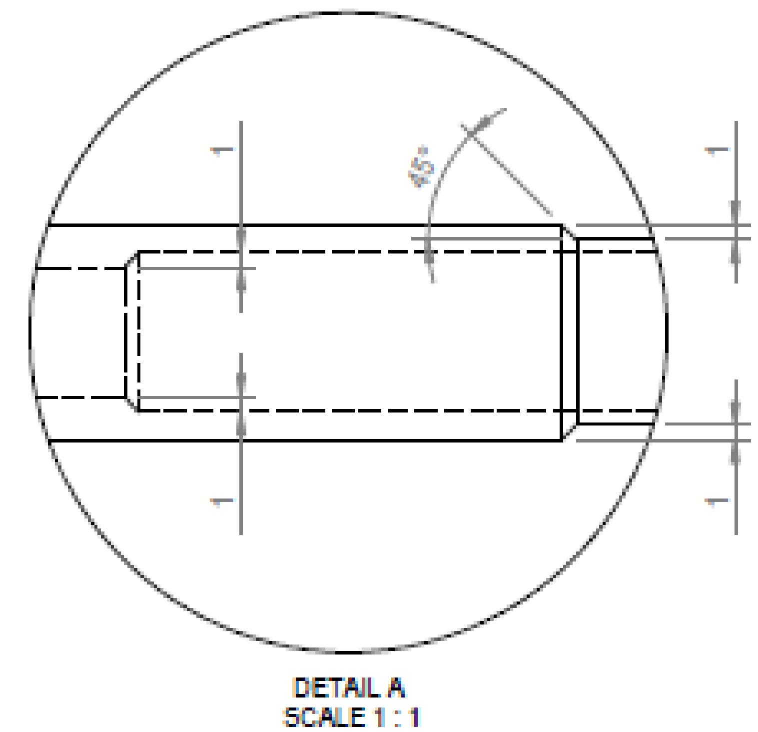
Feature \ Material	SS316L	Ti6Al4V	AlSi10Mg	AlSi7Mg	Invar
Heat Treatment	None	None	400°C, 2 hr dwell	400°C, 2 hr dwell	850°C, 1 hr dwell
Filling tube	2.0 mm ID	4.55 mm ID (welded Ti CP Grade 2 tubing)	2.0 mm ID	2.0 mm ID	4.55 mm ID

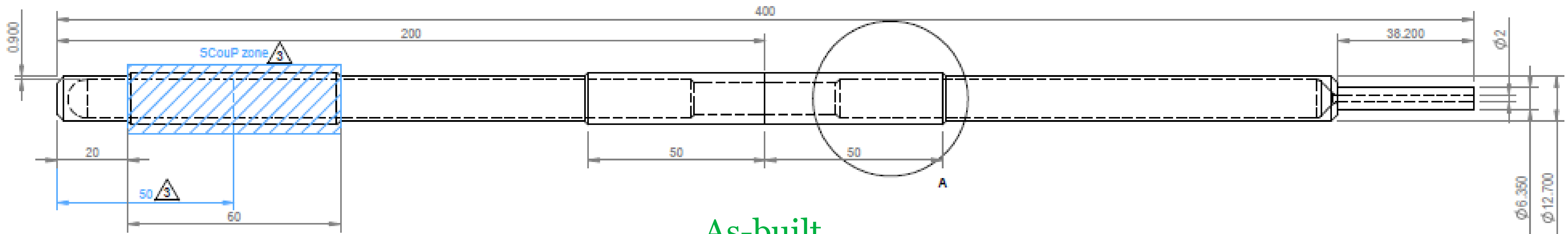
WP2 Test definition

- **ALM coupon testing**
  - Particularly useful exercise due to information gained regarding performance and behaviour of ALM materials necessary for later manufacture.
  - Designs of final thermosyphons were updated in terms of:
    - Filling tube geometry
    - Heat treatments
    - Surface roughness considerations for later welding, sealing and port connections.
  - Unfortunate coupons of Invar could not have been tested at this point due to machine scheduling/ lead times.

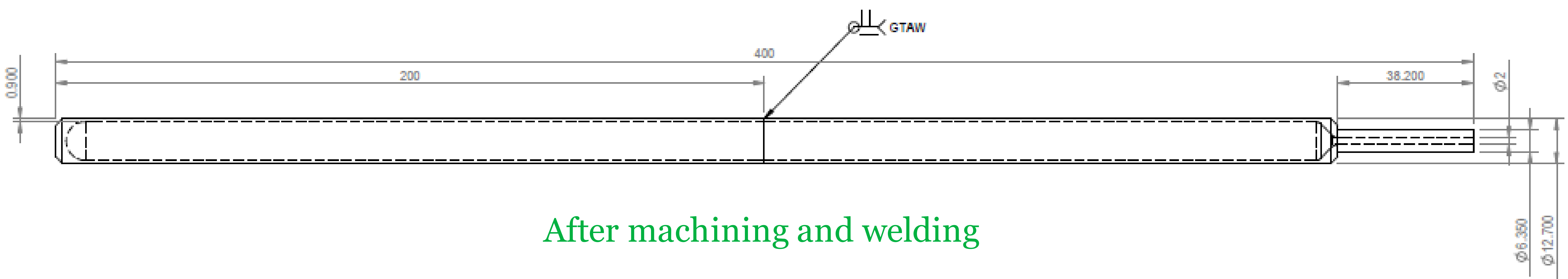
WP2 Test definition

- **Sample design**
  - ALM AlSi7Mg and AlSi10Mg





As-built

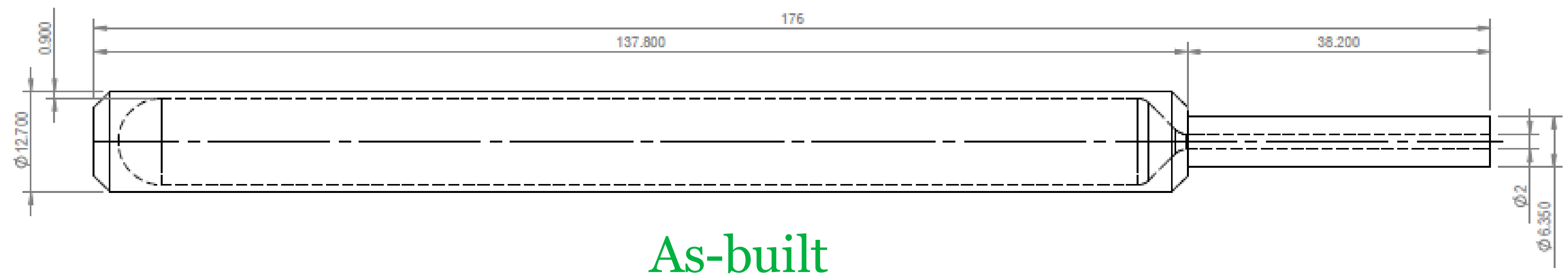


After machining and welding

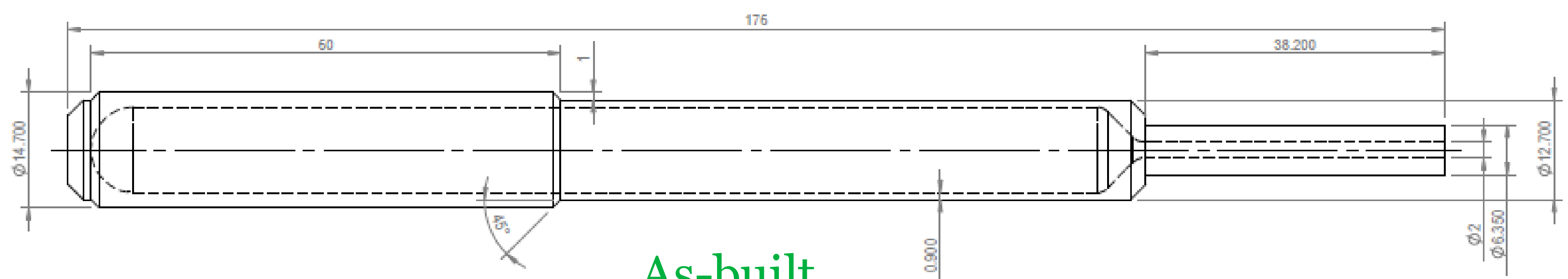
UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH Bernal Institute

WP2 Test definition

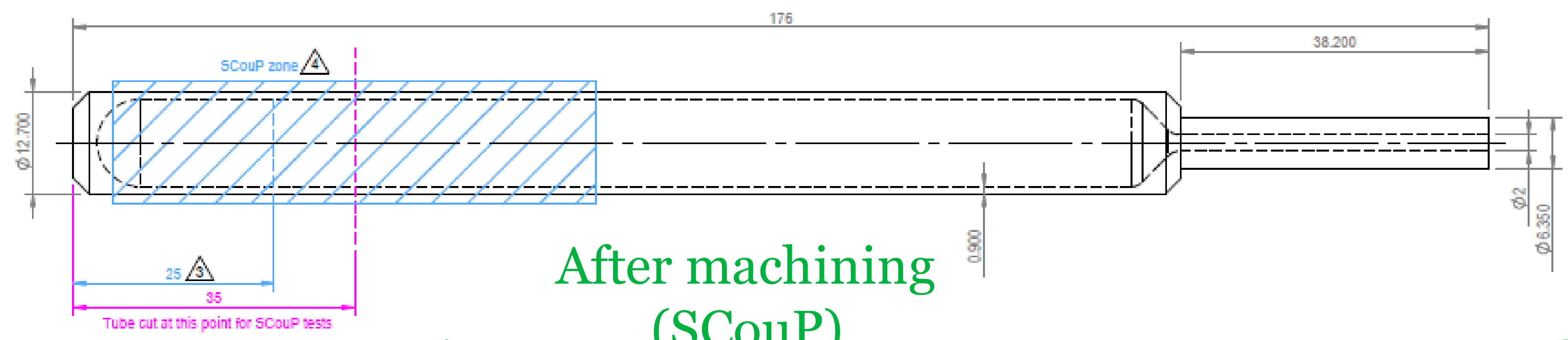
- **Sample design**
  - ALM SS316L



As-built



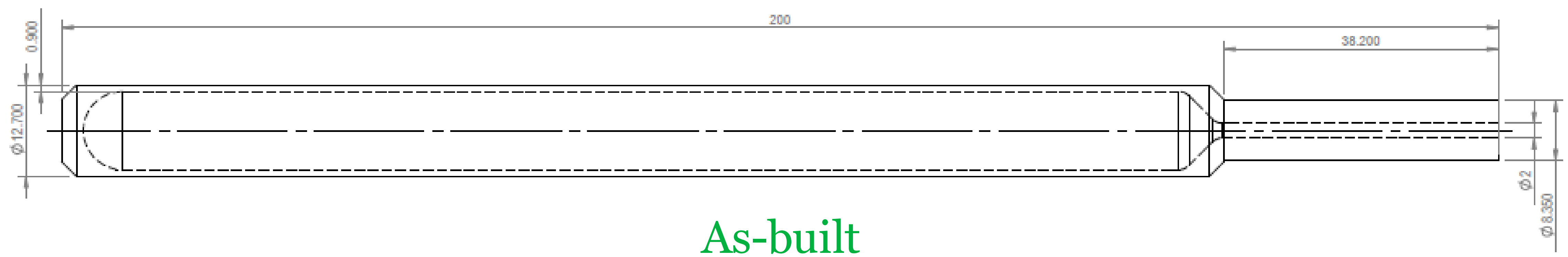
As-built
(SCouP)



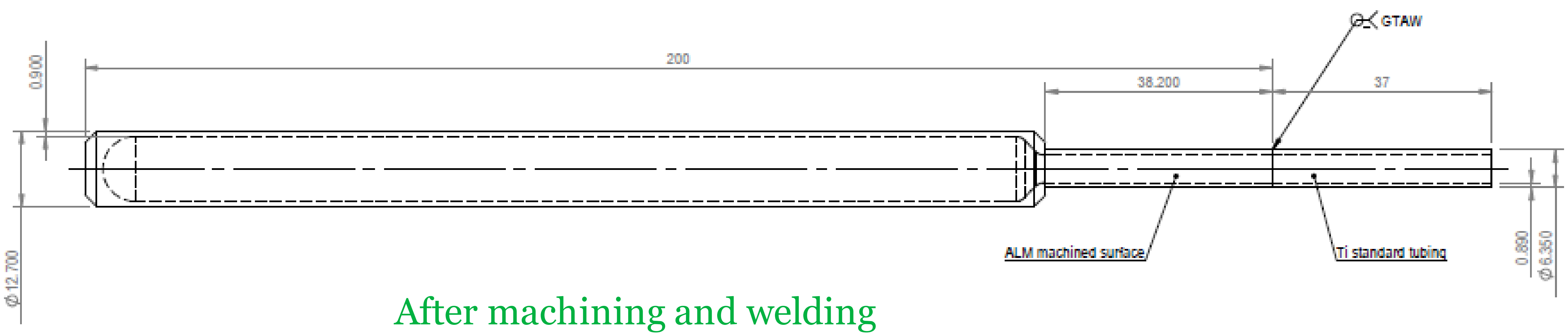
After machining
(SCouP)

WP2 Test definition

- **Sample design**
  - ALM Ti6Al4V



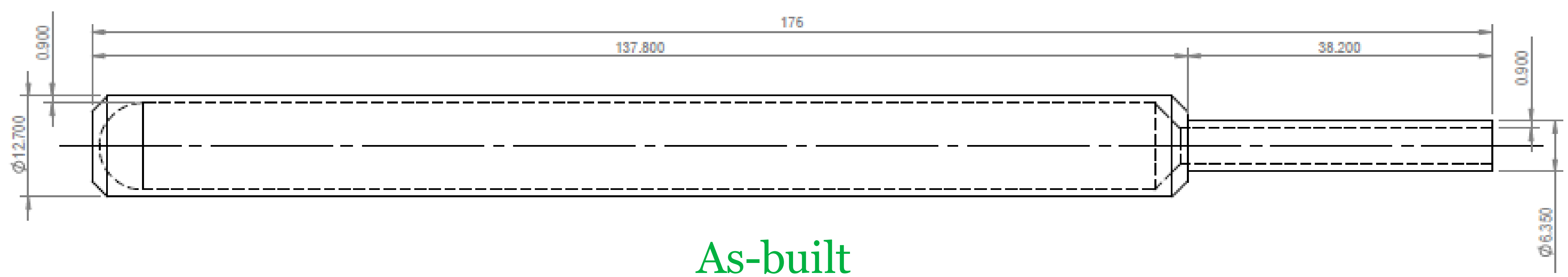
As-built



After machining and welding

WP2 Test definition

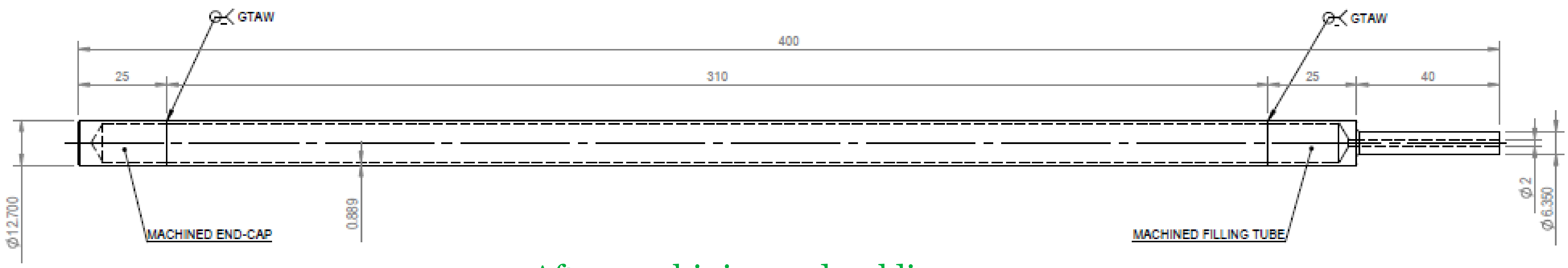
- **Sample design**
  - ALM Invar



As-built

WP2 Test definition

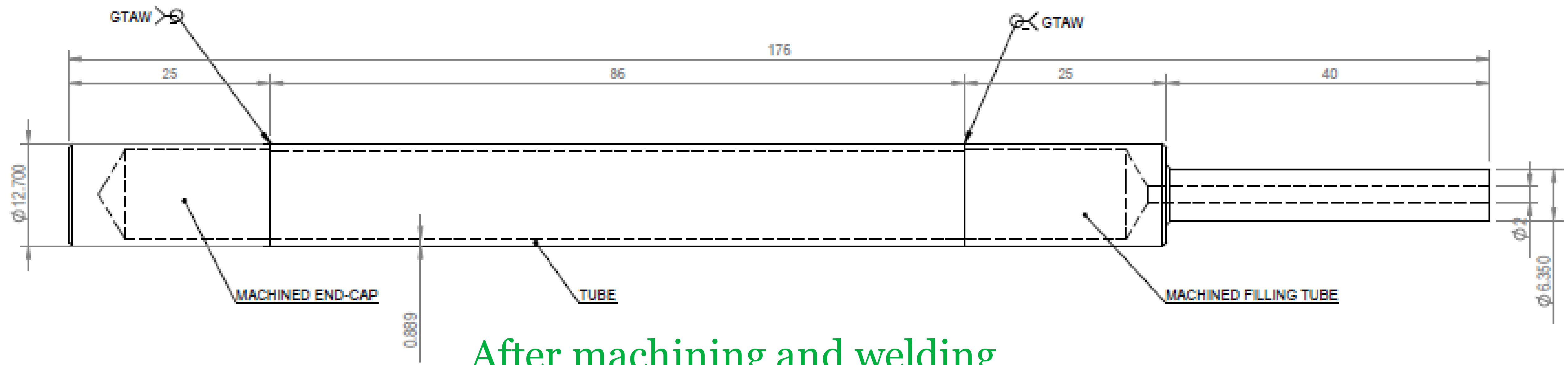
- **Sample design**
  - Al6061 conventional



After machining and welding

WP2 Test definition

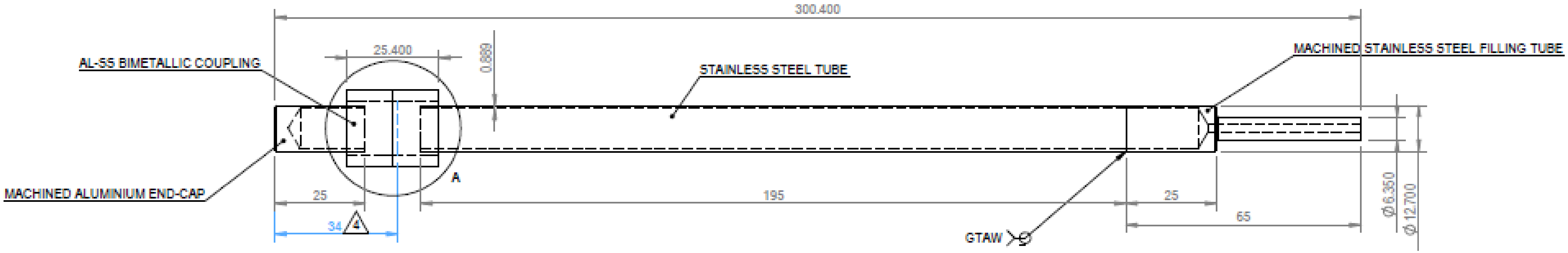
- **Sample design**
  - SS316L conventional

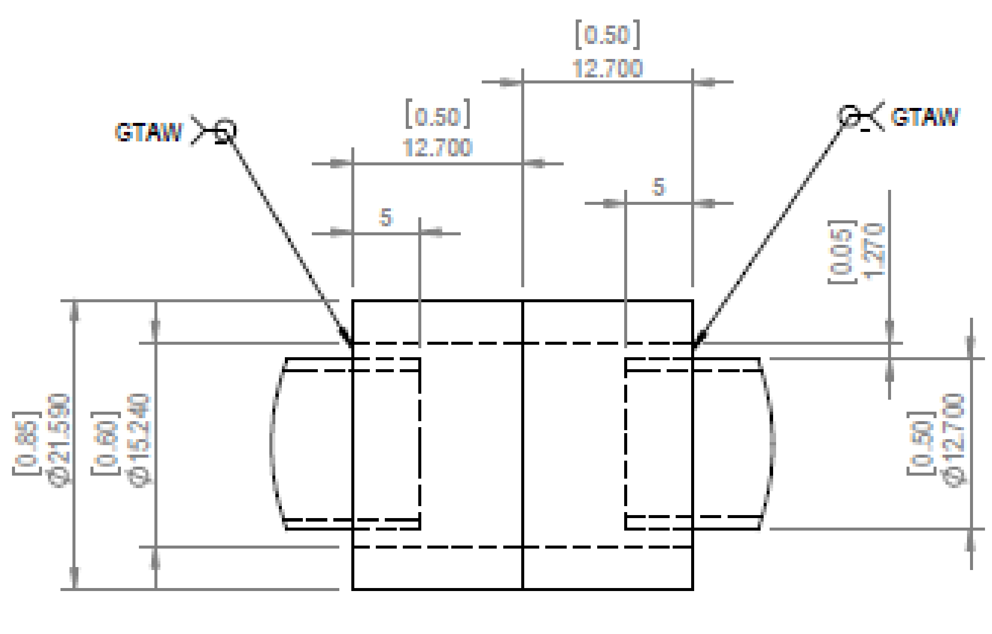


After machining and welding

WP2 Test definition

- **Sample design**
  - Bimetallic Al6061 - SS316L conventional





DETAIL A
SCALE 1 : 1

After machining and welding

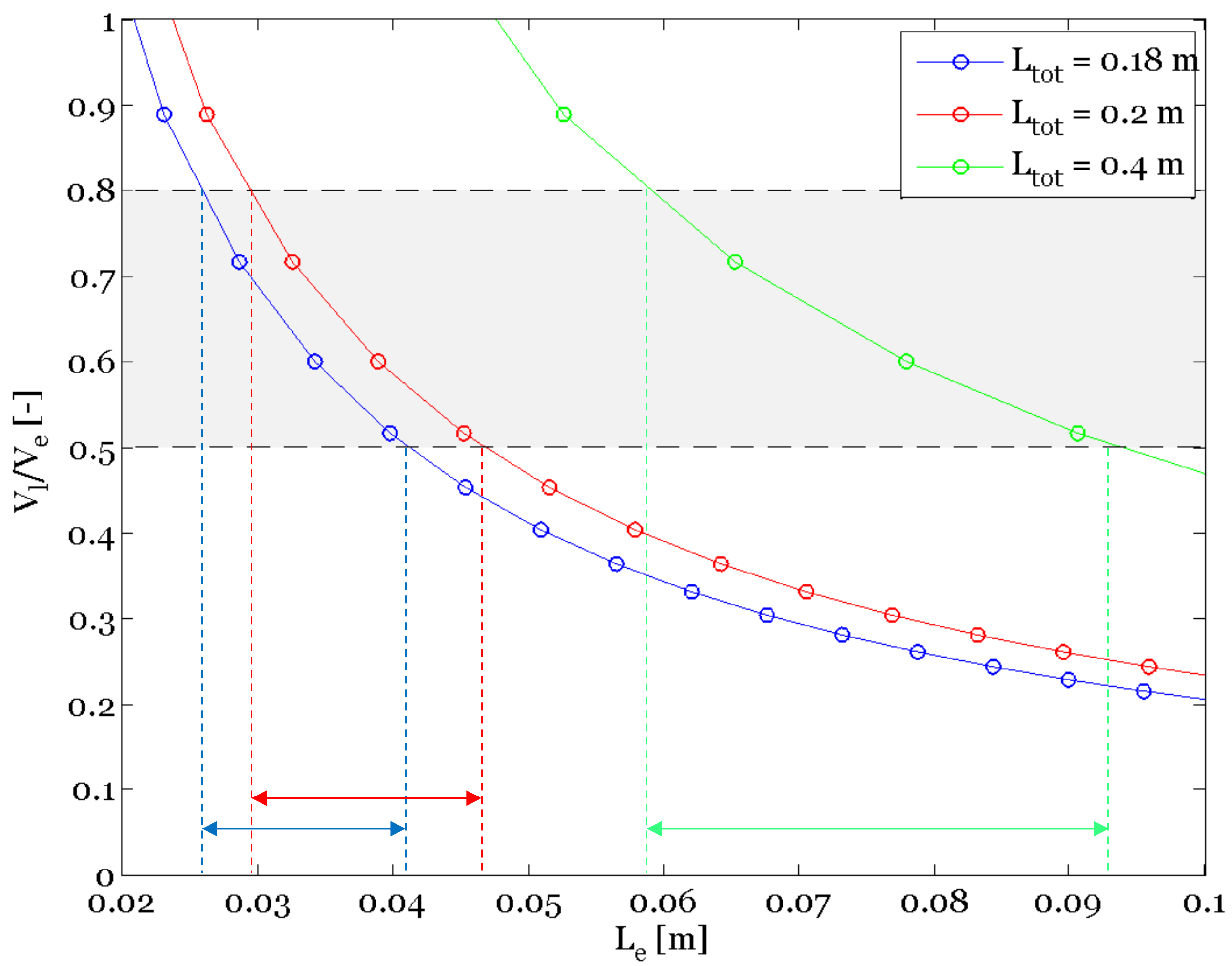
Spur Industries, Inc. roll bonded Al3003– SS304L bi-metallic junction.

WP2 Test definition

- **Filling Volume**
  - For thermosyphon devices, the recommended liquid fill is in the range 50-80% of the volume of the evaporator.
  - Volume of liquid can also be related to thermosyphon dimensions by [*Reay & Kew, 2006*]:

$$V_l > 0.001(d - 2t)(l_e + l_a + l_c)$$

Material	**Tube length [mm]**	**Fill volume [ml]**
Aluminium	400	4.4
Stainless-steel / Invar	176	1.9
Titanium	200	2.2
Al + SS bimetallic coupling	313.4	3.4



WP2 Test definition

- **Filling Volume**
  - Working fluids filling mass at 25°C:

Fluid	Filling mass [g]			
	1.9 ml	**2.2 ml**	**3.4 ml**	**4.4 ml**
Ammonia	1.15	1.33	2.05	2.65
Acetone	1.49	1.73	2.67	3.45
Ethylene glycol	2.11	2.44	3.77	4.88
Methanol	1.49	1.73	2.67	3.46
Propylene	0.96	1.11	1.72	2.23
Toluene	1.64	1.90	2.93	3.79
Water	1.89	2.19	3.39	4.39

WP2 Test definition

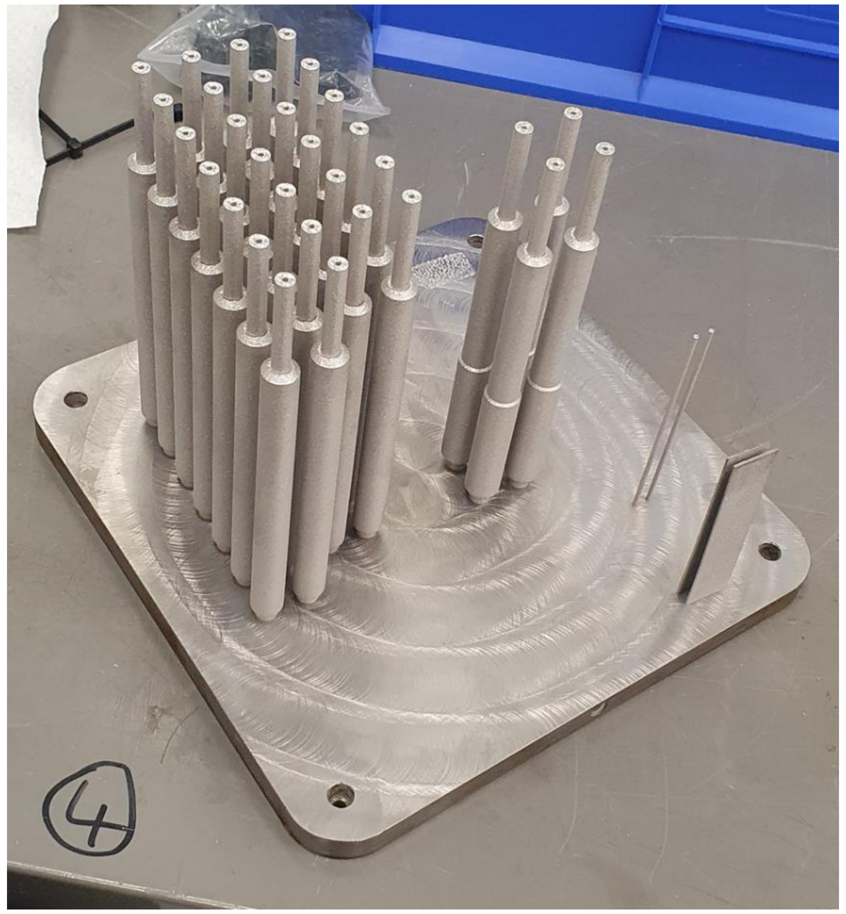
- Additional definitions and specifications regarding:
  - Proof Pressure testing
  - Helium leak testing
  - Sealing
  - Fluid purity
  - Gas plug testing

  presented in following relevant manufacturing sections.

WP3 Manufacture

- **Sample manufacture**
  - ALM parts printed by selected suppliers.

Ti6Al4V



SS316L

AlSi10Mg

Invar

WP3 Manufacture

- **Sample manufacture**
  - **Machining** of ALM and Conventional materials performed by UL engineering workshop.

Ti6Al4V

AlSi7Mg / AlSi10Mg

AlSi7Mg / AlSi10Mg
for SCouP

SS316L
for SCouP

Al6061 and SS316L end caps and filling tubes

WP3 Manufacture

- **Sample manufacture**
  - **Welding** performed by Southern Steel Engineering, IE.
    - **SS316L:** Orbitally welded with DC inverter, pulsed current 33 A/14 A.
    - **Ti6Al4V:** Orbitally welded with DC inverter, 25 A, argon shielding gas.
    - **Al6061/AlSi7Mg/AlSi10Mg:** Manually TIG welded, AC power source, 60Hz 18-23 A, 4043 filler wire, PC welding position.
    - **Al-SS bimetallic:** Al side manually TIG welded, DC inverter, 58 A, 316L filler wire.
  - Argon N5.0 shielding and purge gas used in all cases.

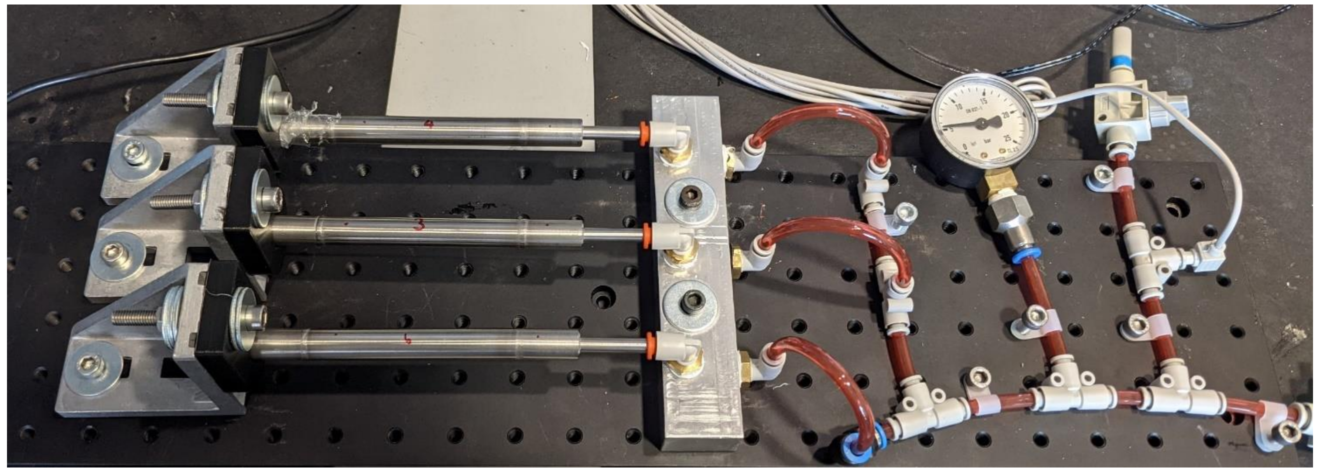
  - Al samples wall thickness and diameter was difficult to manually TIG weld. No significant difference between conventional and ALM alloys.
  - Bimetallic sample was particularly difficult to weld due to size and fit of coupling compared to tubing diameter and thickness.


SS316L
Al6061
SS316L
Invar
Ti6Al4V
AlSi7Mg/AlSi10Mg
Bimetal.
SS316L
AlSi7Mg/AlSi10Mg
Conventional
ALM
SCouP

WP3 Manufacture

- **Sample testing**
  - **Proof Pressure**
    - **High vapour pressure fluids**
    - Hydrostatic testing at 30 bar(g) (1.5 x MDP) for samples intended for ammonia and propylene.
    - Hold time of 15 minutes (as per ECSS-E-ST-31-02C).
    - Pressure recording by DLP-A19 transducer.
    - Swagelok compression fitting used for connection to test rig.

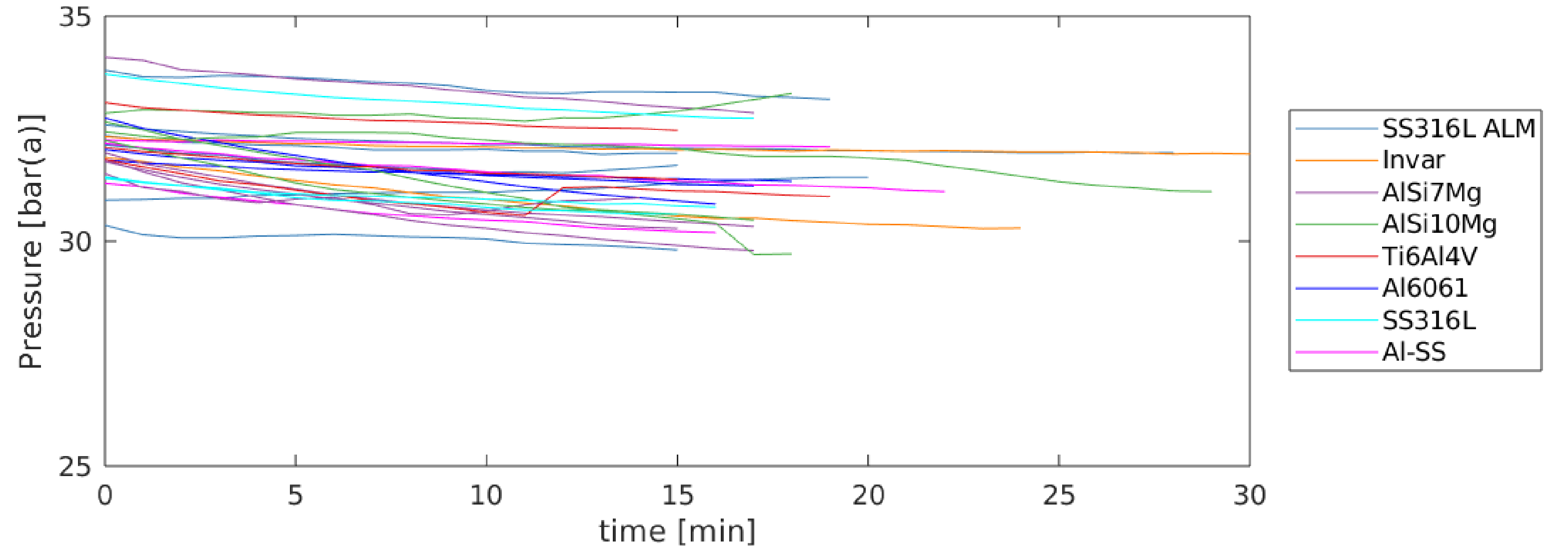
- **Low vapour pressure fluids**
- Pneumatic (air) testing at 6 bar(a) (1.5 x MDP) for samples intended for acetone, methanol, toluene, water, ethylene glycol (max. 1.5 x MDP is 5.6 bar(a) for acetone).
- Hold time of 15 minutes (as per ECSS-E-ST-31-02C).
- Pressure recording by PSE540A transducer.



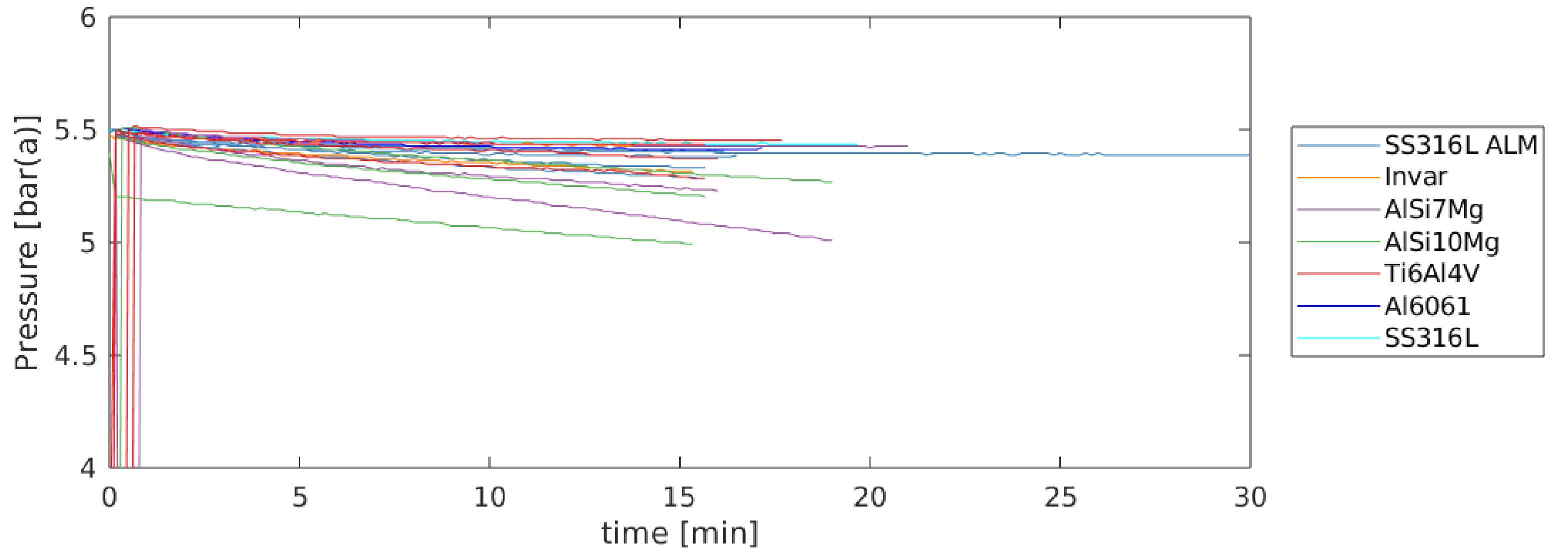
WP3 Manufacture

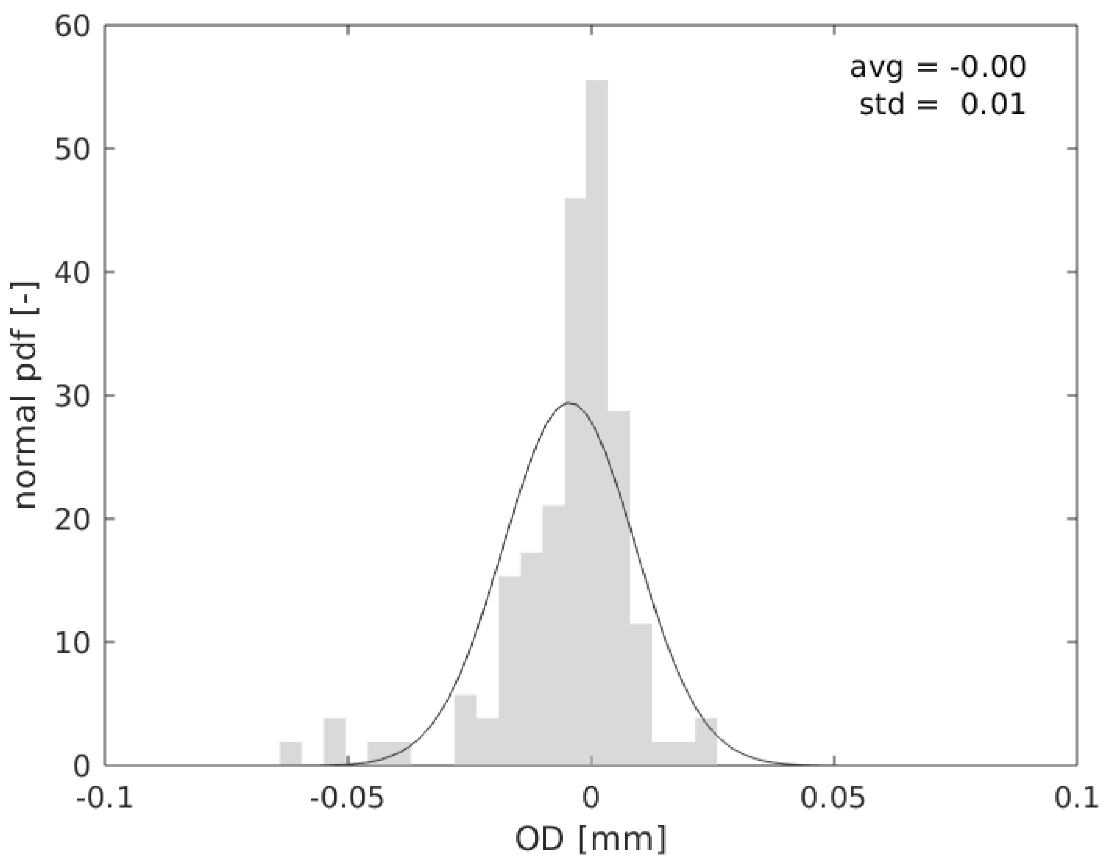
- **Sample testing**
  - **Proof Pressure**
    - Negligible change in OD before and after. Main variation due to surface roughness.

Hydrostatic



Pneumatic

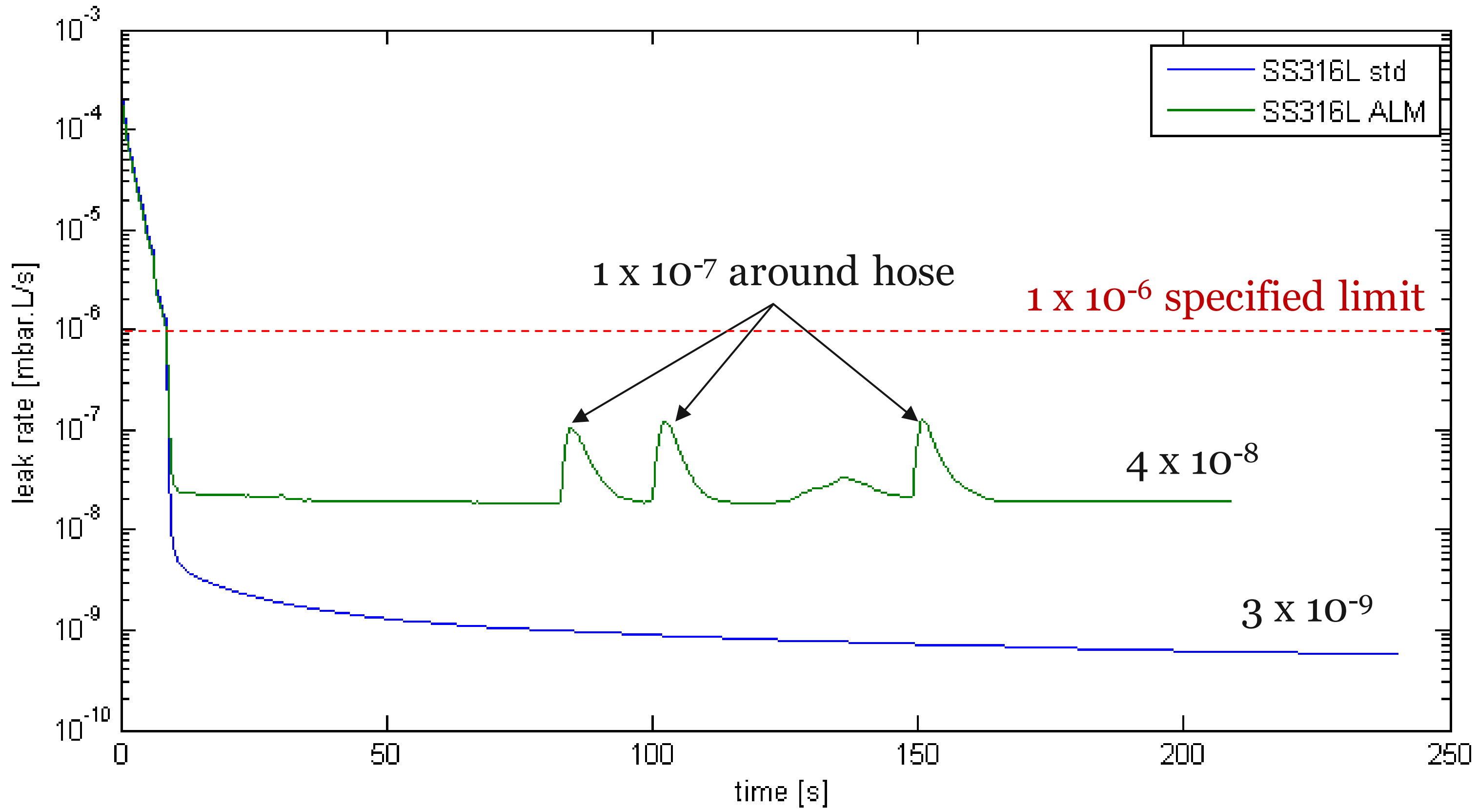


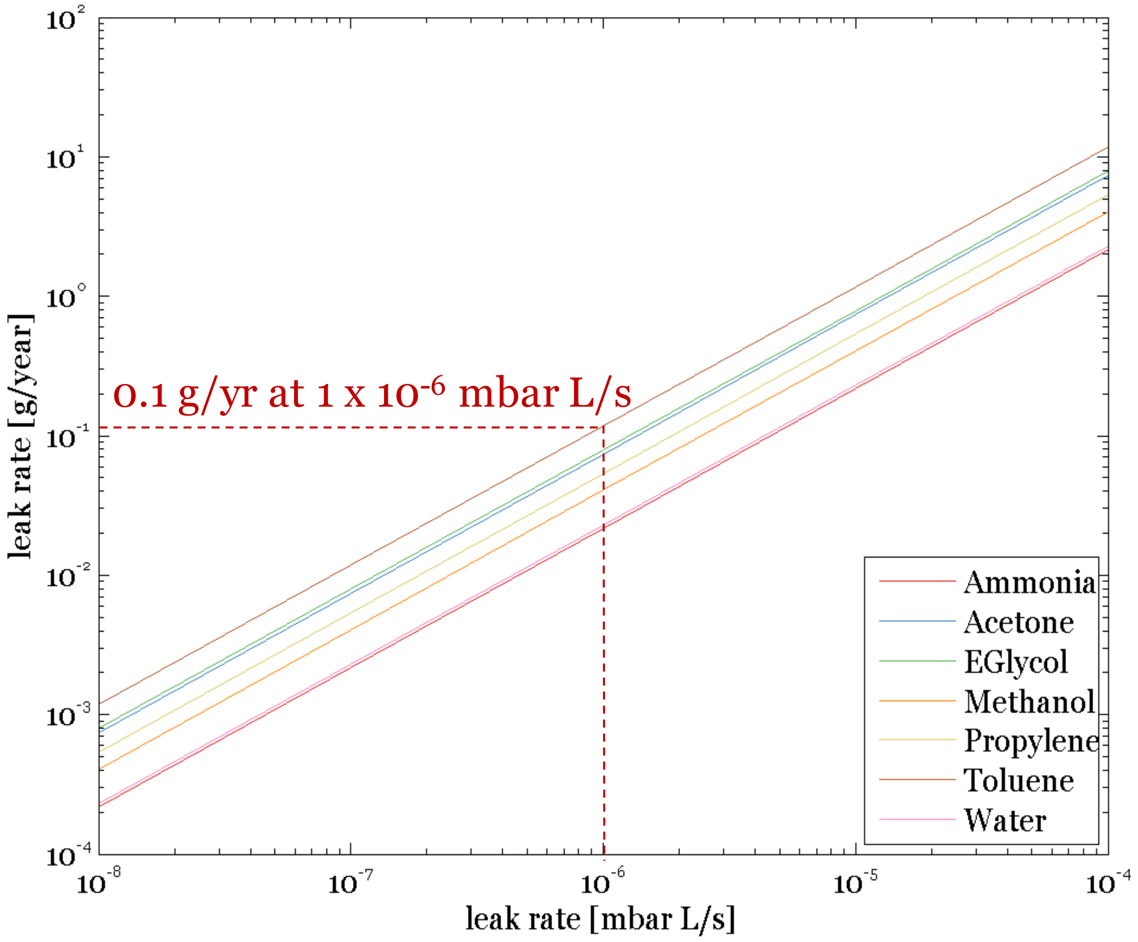


UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

WP3 Manufacture

- **Sample testing**
  - **He Leak**
    - Performed using a Leybold Vario leak detector in vacuum/spray mode.
    - Due to surface roughness of ALM parts, a rubber hose was used to connect the samples to the leak detector.



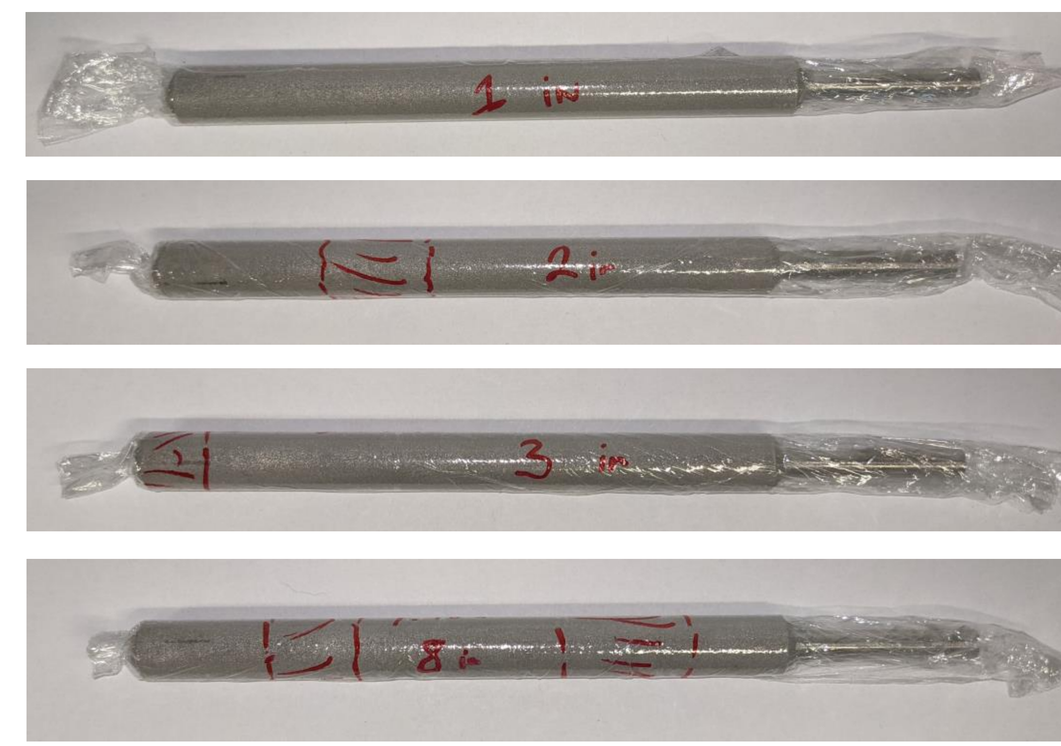


- All tubes which passed had a baseline leak rate of 5×10^{-9} mbar.L/s, including around Swagelok fitting.

WP3 Manufacture

- **Sample testing**
  - **He Leak - Invar**
    - 8/12 samples failed in various locations across tubes.

Sample No.	Pass	Fail	Comments
1	✓		
2		X	6.0×10^{-5} mbar.L/s failed in the middle
3		X	3.4×10^{-5} mbar.L/s failed on end cap
4	✓		
5		X	2.0×10^{-1} mbar.L/s failed on end cap
6		X	1.6×10^{-1} mbar.L/s failed on end cap
7		X	1.1×10^{-3} mbar.L/s failed on end cap
8		X	1.0×10^{-2} mbar.L/s failed in two locations
9		X	Failed to pump down
10		X	2.0×10^{-1} mbar.L/s failed on end cap
11	✓		
12	✓		



WP3 Manufacture

- **Sample testing**
  - **He Leak - Invar**
    - Most leaks were usually around end cap

VS.

Invar

SS316L

AlSi7Mg

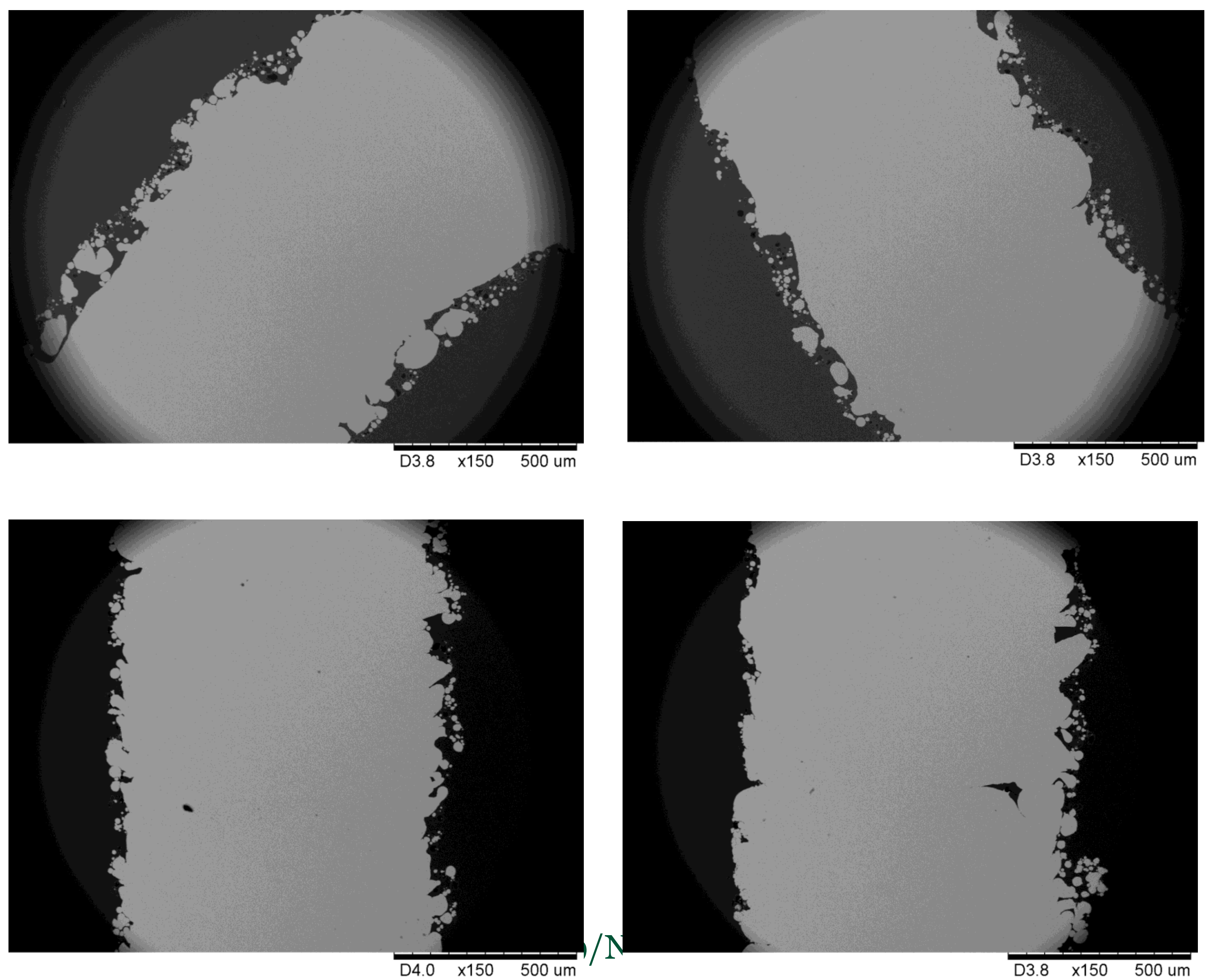
WP3 Manufacture

- **Sample testing**
  - **He Leak - Invar**
    - SEM imaging
    - Measured wall thickness of ~0.85 mm which is within +/- 0.15 mm ALM tolerance.

radial

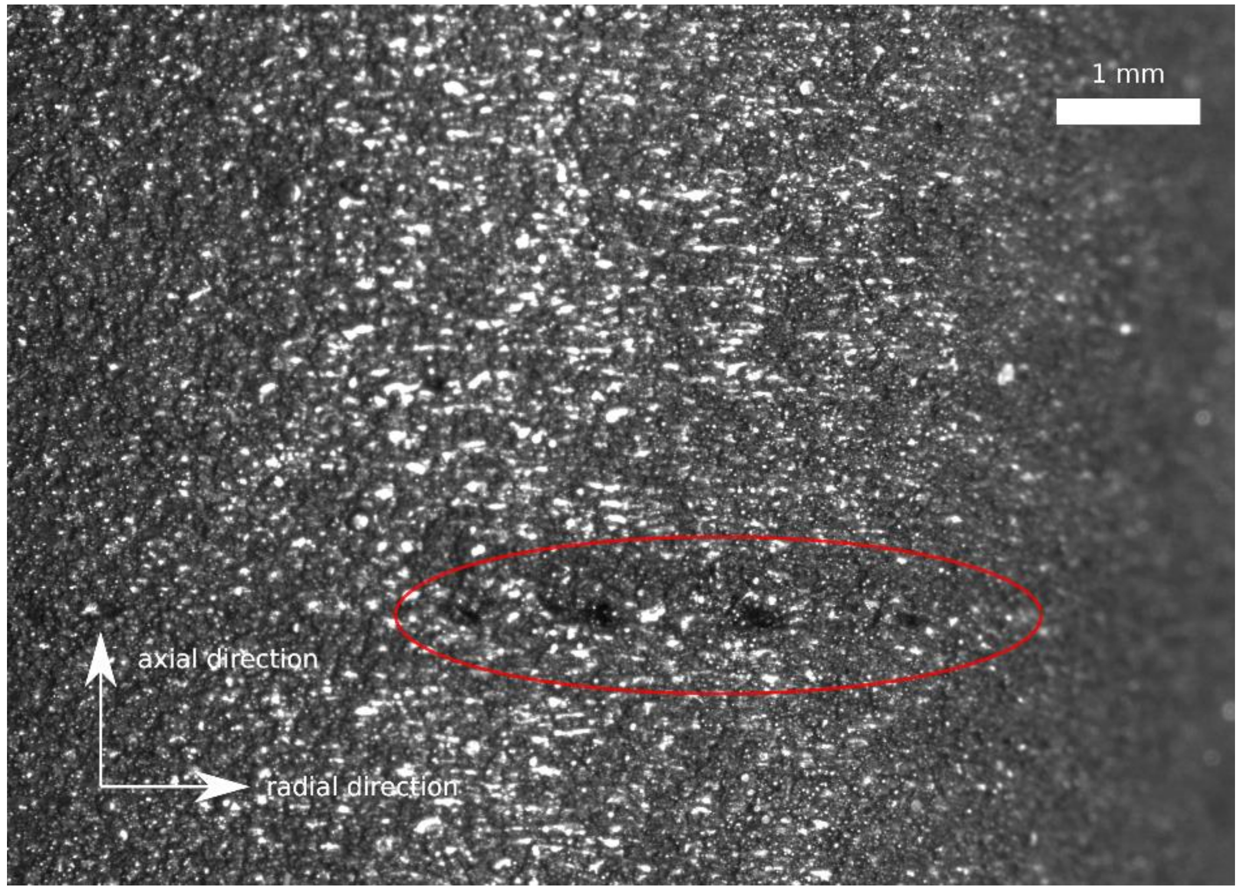
x 150
(1.1 µm/px)

longitudinal



WP3 Manufacture

- **Sample testing**
  - **He Leak - Invar**
    - Bubble test + Microscope imaging



Build direction

- Non-leaking samples subjected to proof pressure testing at 30 bar and passed.

UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

WP3 Manufacture

- **Sample pre-fill cleaning**
  - Numbers engraved on each part for traceability.
  - During each manufacturing step, all parts were cleaned in ultrasonic bath with IPA.
  - Final cleaning steps before filling were taken from
    - ISO 27831:2008 – 1 & 2 (*Cleaning and preparation of metal surface – Ferrous and non-ferrous metals and alloys*)
    - ASTM B600:2011 (*Descaling and Cleaning of Titanium and alloys*)
    - ASTM A967:2005 (*Chemical Passivation Treatment of Stainless Steel parts*)

STEP 1:	STEP 2:	STEP 3:
Light scouring of welded areas with fine alumina pads (maroon *Scotch-Brite*)	Ultrasonic cleaning with GC grade (>99.5%) 2-Propanol	Rinse in de-ionised water

  - Parts positioned horizontally and vertically to remove any ALM powder.
  - IPA changed between each material.

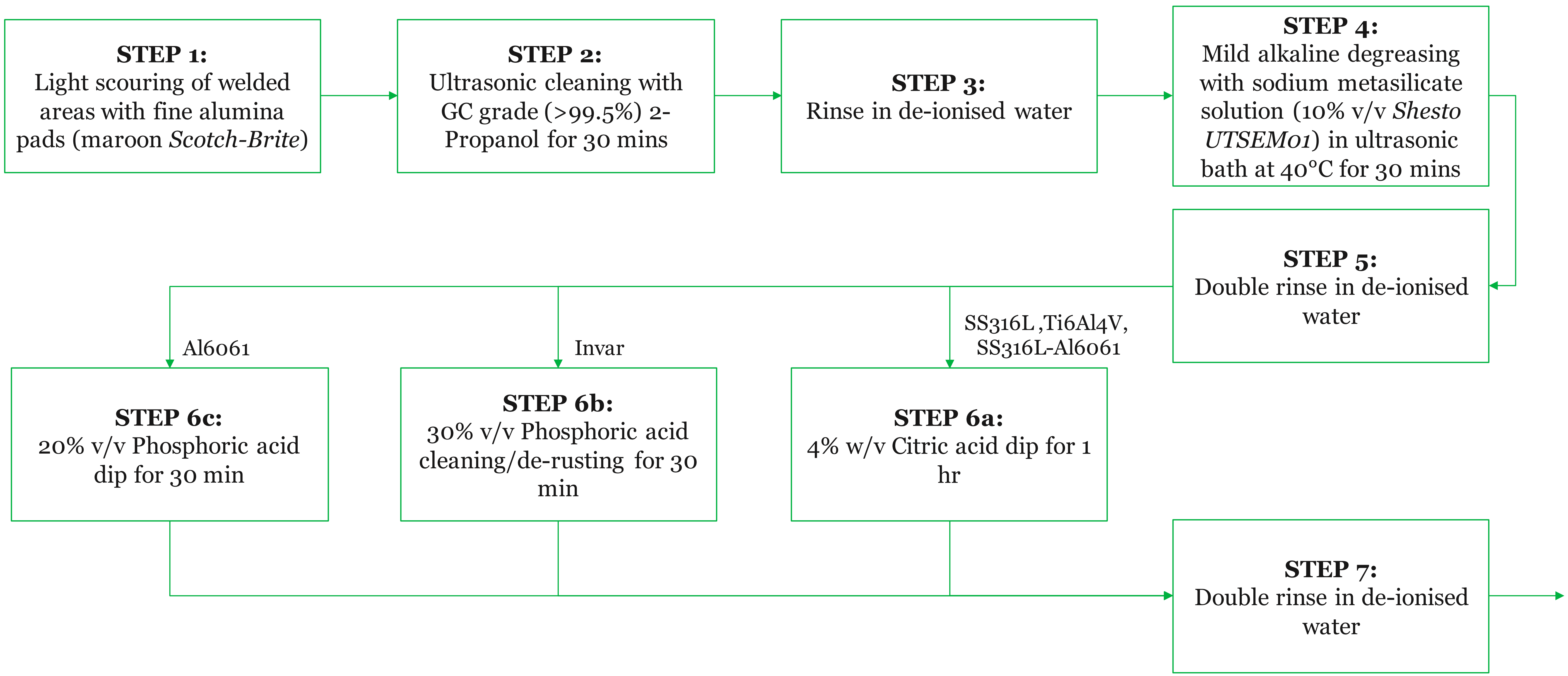
Grant XB3 for short samples (238 x 135 x 100 mm, L x W x D)

Sonorex RK1050-CH for long samples (600 x 500 x 300 mm)

UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

WP3 Manufacture

- **Sample pre-fill cleaning**



UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

WP3 Manufacture

- **Sample pre-fill cleaning**
    - Acid cleaning is unsuitable for aluminium alloys with a mass fraction of 2% or more of silicon.

→ **STEP 7:** Double rinse in de-ionised water → **STEP 8:** Dried with compressed air → **STEP 9:** Placed in vacuum drying oven at 50°C overnight → **STEP 10:** Parts are capped

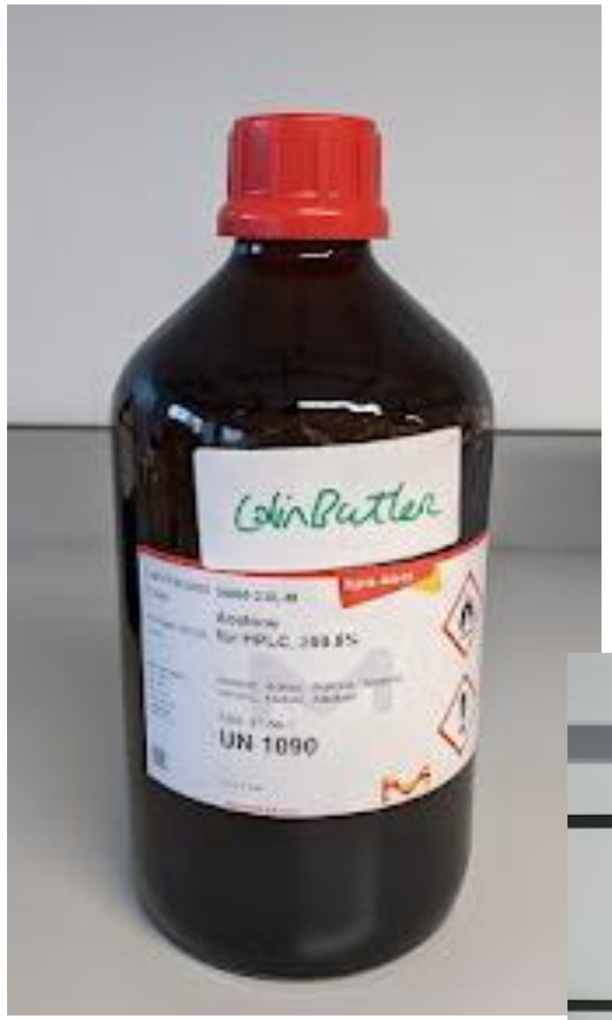
WP3 Manufacture

- **Sample pre-fill cleaning**
  - Rinsing of closed-end samples through 2.0 mm filling tube was particularly challenging and required multiple rinses.
  - All cleaning steps were performed following each other with minimum delay.
  - Parts were cleaned in batches to minimise delay before filling.

WP3 Manufacture

- **Sample filling**

Fluid	State at STP	Supplier	Product Number	Purity / Grade
Acetone	Liquid	Sigma-Aldrich	34850	≥99.9% (HPLC, GC grade)
Ammonia	Gas	Sigma-Aldrich	294993	99.98% (anhydrous grade)
Ethylene glycol	Liquid	Sigma-Aldrich	102466	99.4% (ReagentPlus Grade)
Methanol	Liquid	Sigma-Aldrich	34860	≥99.9% (HPLC, GC grade)
Propylene	Gas	Sigma-Aldrich	295663	≥99.9%
Toluene	Liquid	Sigma-Aldrich	650579	≥99.9% (HPLC, GC grade)
Water	Liquid	Sigma-Aldrich	270733	HPLC grade



2.5 L bottle of Acetone

300 g cylinder of Ammonia

WP3 Manufacture

- **Sample filling**
  - 2 configurations of one station to perform filling for liquids and gases.
  - Order of fluid filling was selected based on "easiest"/lowest risk to equipment:

Fluid	No. of combinations	No. of tubes
Water	2	6
Methanol	3	8
Acetone	4	12
Toluene	5	15
Propylene	3	9
Ammonia	11	32
Ethylene glycol	5	15

  - Filling rig is baked-out between fluids.
  - New glassware was used for degassing flask when changing fluids.

WP3 Manufacture

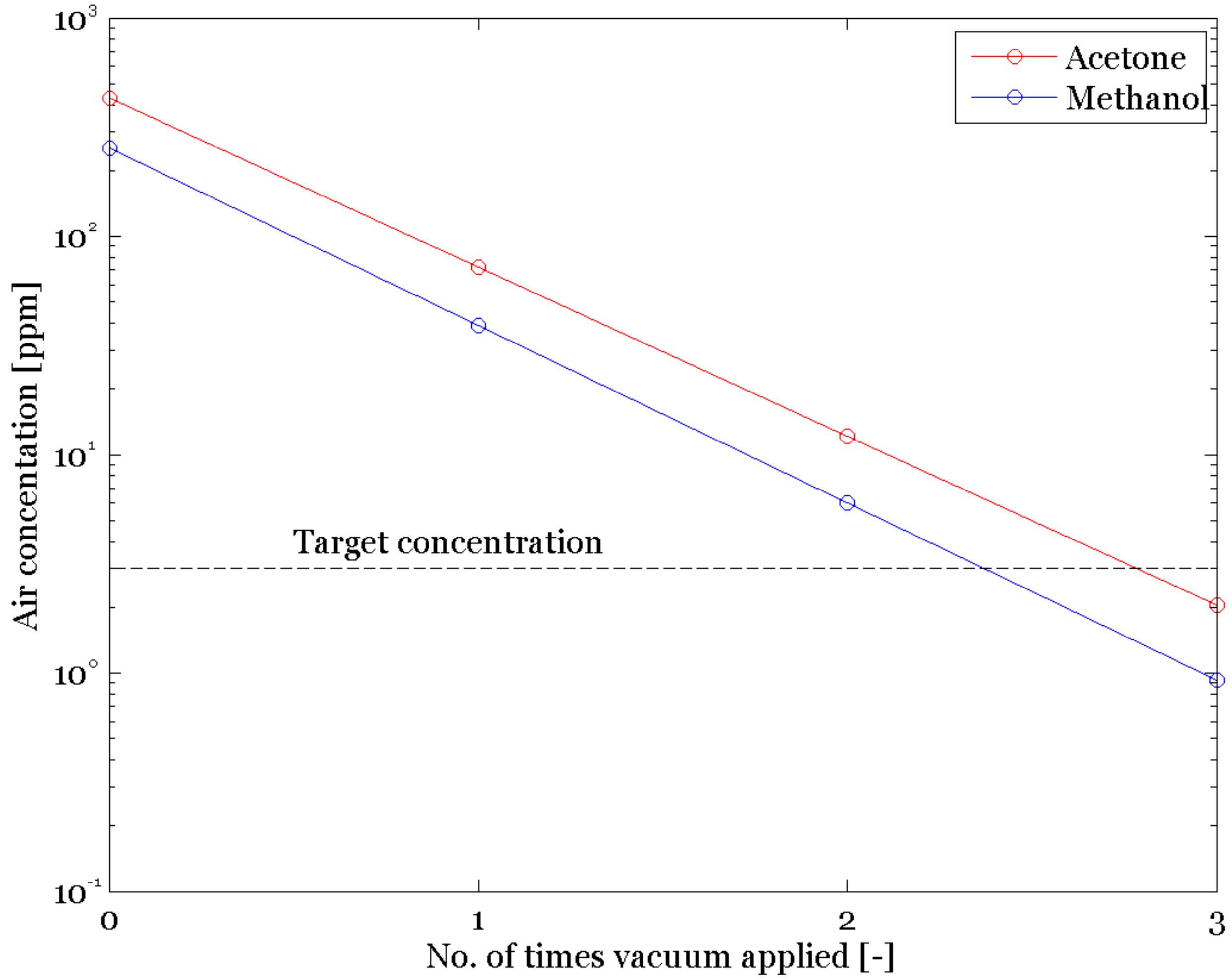
- **Sample filling**
  - **Liquids**
  - Degassing of liquids for use in two-phase heat transfer devices typically include boiling and vacuum degassing.
  - If the vapour and air above a liquid inside a closed container are removed using a vacuum pump, assuming the liquid volume does not change, the air contained in the liquid must come out of solution to fill the evacuated volume [*Henry, et al., 2005*].
  - The reduction in partial pressure of the air above the liquid before and after applied vacuum is:

$$\frac{P_{a,i+1}}{P_{a,i}} = \frac{H(T)\rho_l V_l \frac{M_a}{M_l}}{\frac{V_g}{R_a T} + H(T)\rho_l V_l \frac{M_a}{M_l}}$$

  - where $P_{a,i}$ is the initial partial pressure of air above the liquid, $P_{a,i+1}$ is the partial pressure of air after the vacuum has been applied, ρ_l is the density of the liquid, V_l and V_g are the liquid and gas volumes respectively, M_a and M_l are the molecular weights of the air and liquid, respectively, and R_a is the specific gas constant for air.

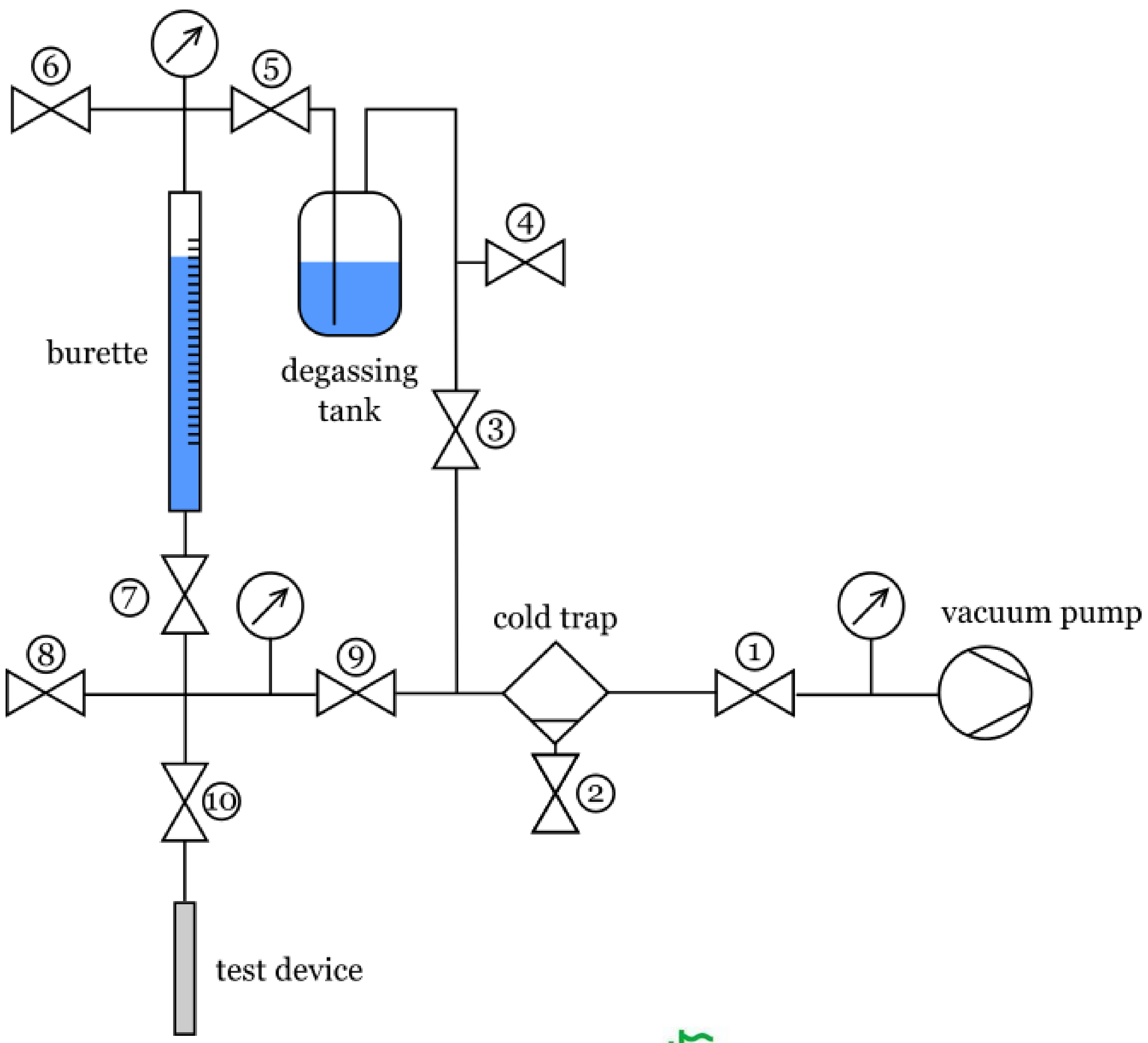
WP3 Manufacture

- **Sample filling**
  - **Liquids**
  - E.g., for Acetone and Methanol where:
    - Container is half-filled with liquid.
    - Initial pressure of 1013 mbar.
    - Fluid properties at 25°C.
    - Target concentration of air of 3 ppm.
  - => Vacuum needs to be applied min. of 3 times.



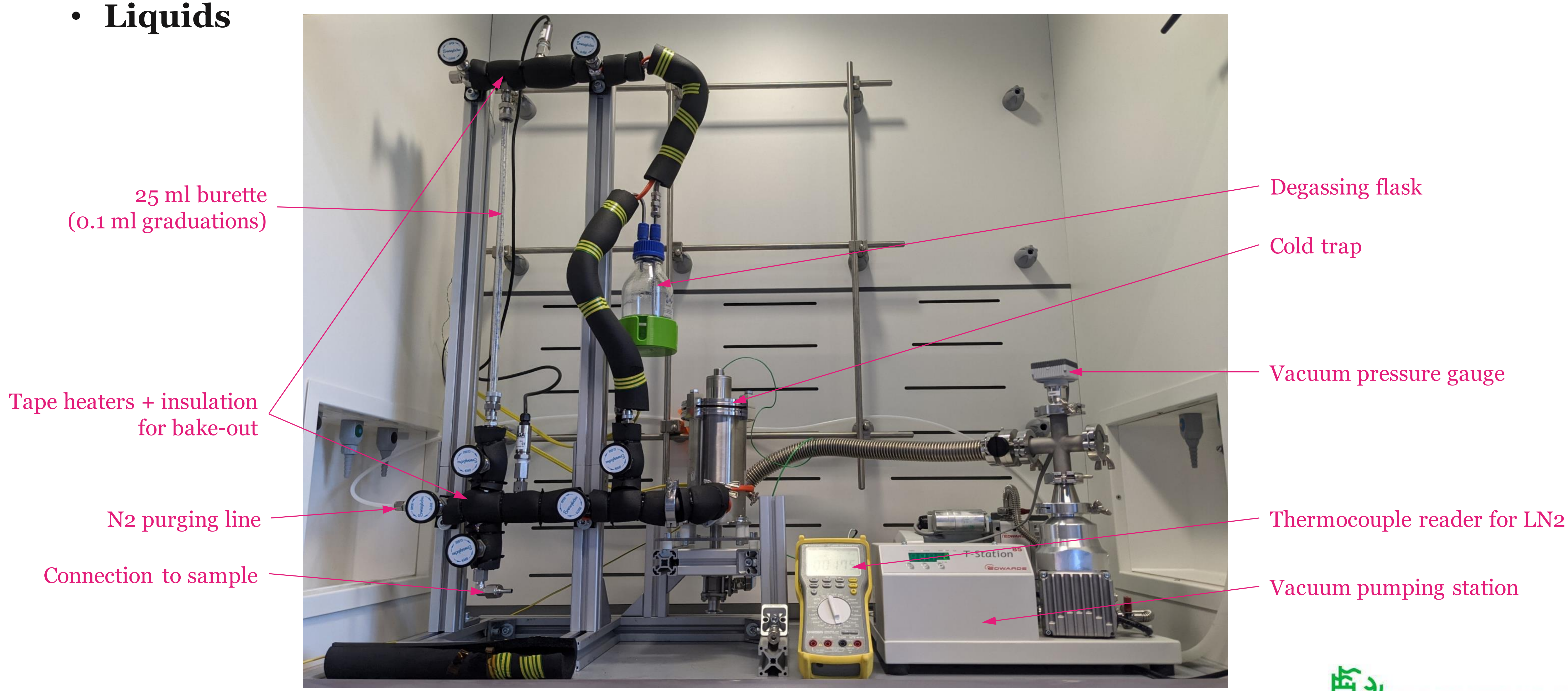
WP3 Manufacture

- **Sample filling**
  - **Liquids**
  - KF and Ultra-torr fittings used for vacuum seals.
  - VCR fittings used for positive and vacuum seals.
  - FFKM O-rings used for chemical compatibility.
  - Edwards Turbo Pumping T-Station 85H used for evacuation and fluid degassing (ultimate vacuum level of < 5×10^{-8} mbar).
  - Edwards APGX-H-NW25 linear convection gauge (3×10^{-4} - 1333 mbar range) used to monitor vacuum level.
  - Omega PX309-300A5V pressure transducers used to monitor vapour and hydrostatic pressures (0 - 21 bar(a) range).
  - LN2 cold trap to prevent fluid entering pump.
  - PID-controlled trace heating tape used for bake-out
  - Installed in fume cupboard for safety.



WP3 Manufacture

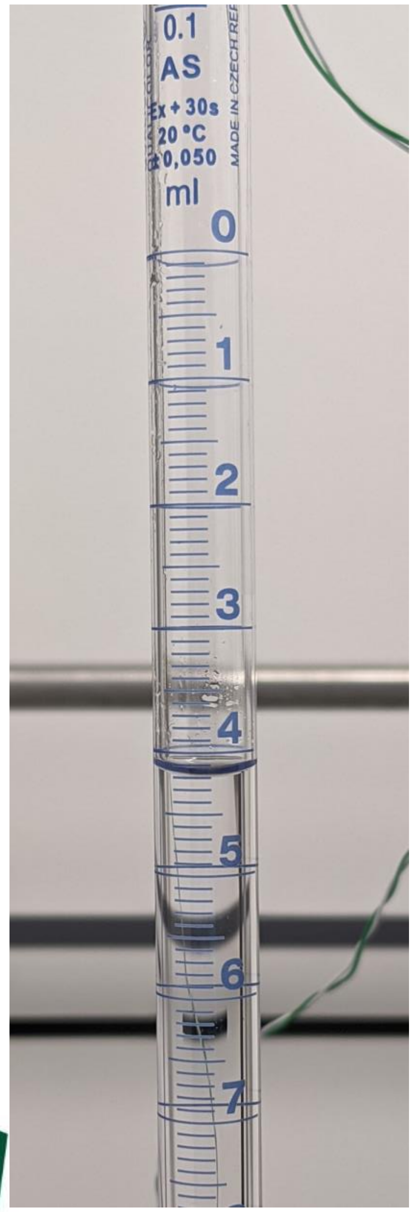
- **Sample filling**
  - **Liquids**



UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

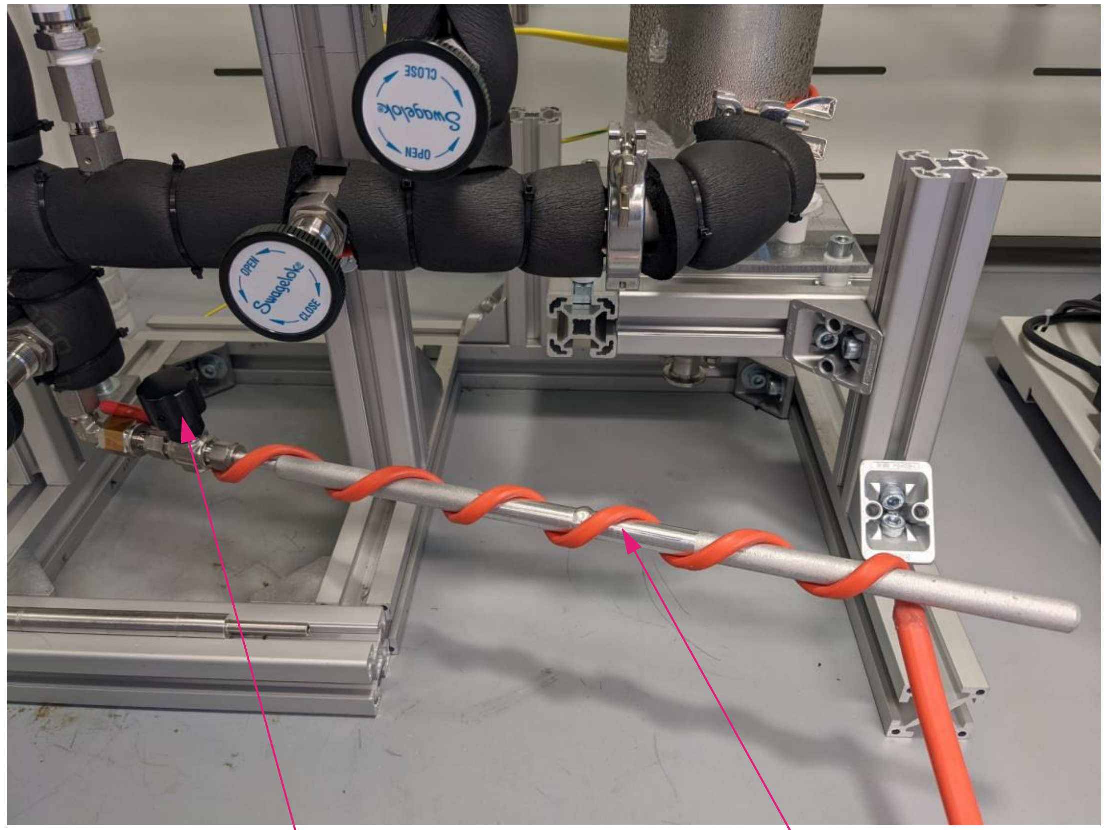
WP3 Manufacture

- **Sample filling**
  - **Liquids**



Glass burette

Feedthrough port for heater PID controllers and pressure transducers



Valve used for connecting to rig

Aluminium ALM sample fitted with heating tape

WP3 Manufacture

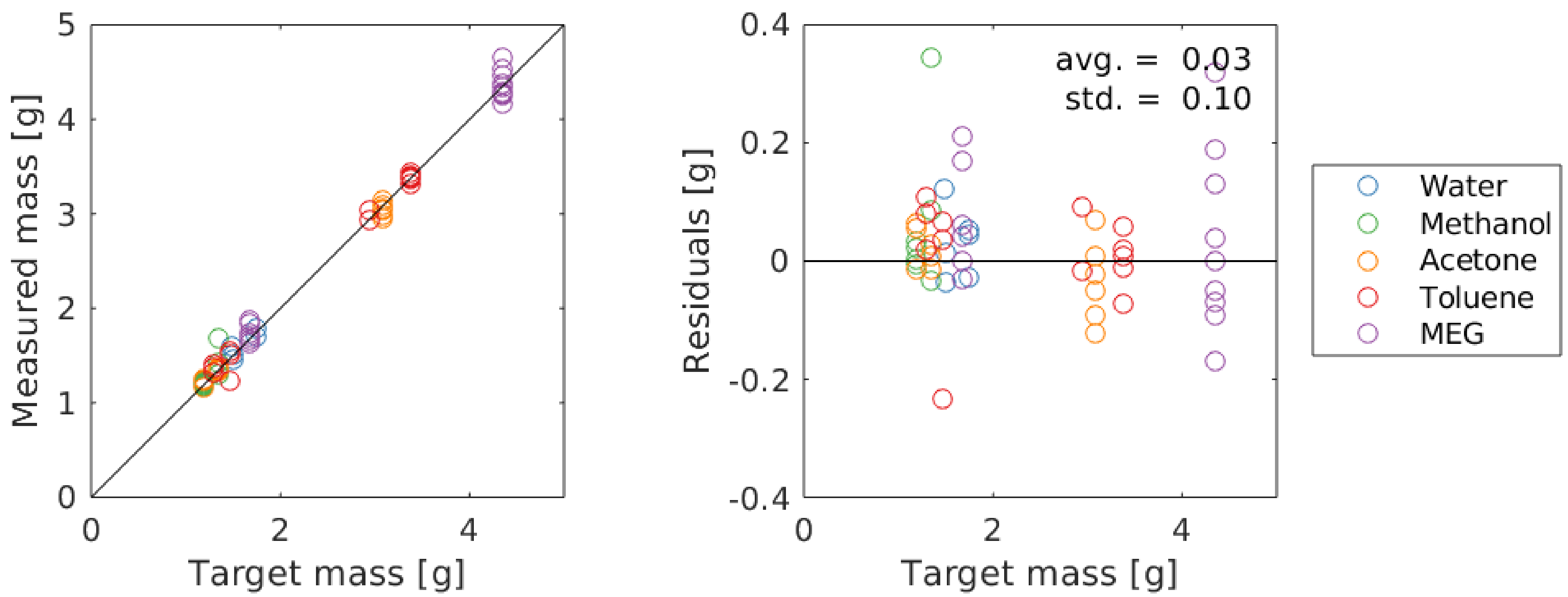
- **Sample filling**
  - **Liquids**

Liquid outgassing

Liquid boiling

WP3 Manufacture

- **Sample filling**
  - **Liquids**
  - Filled working fluid mass was verified by weighing sample before and after.



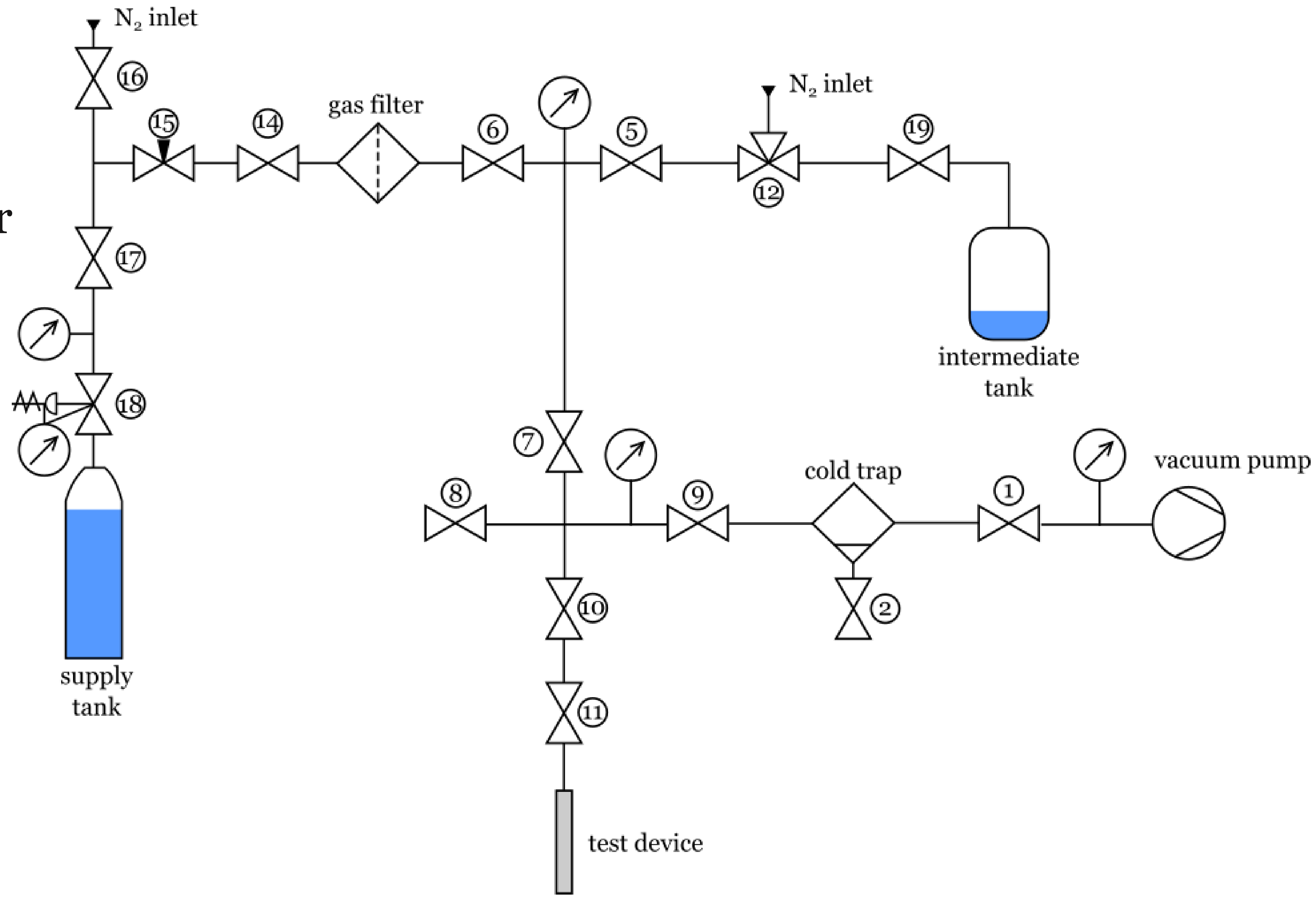
  - Very good accuracy and precision was achieved, with an average difference of 0.03 g and a standard deviation of 0.1 g.

UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

WP3 Manufacture

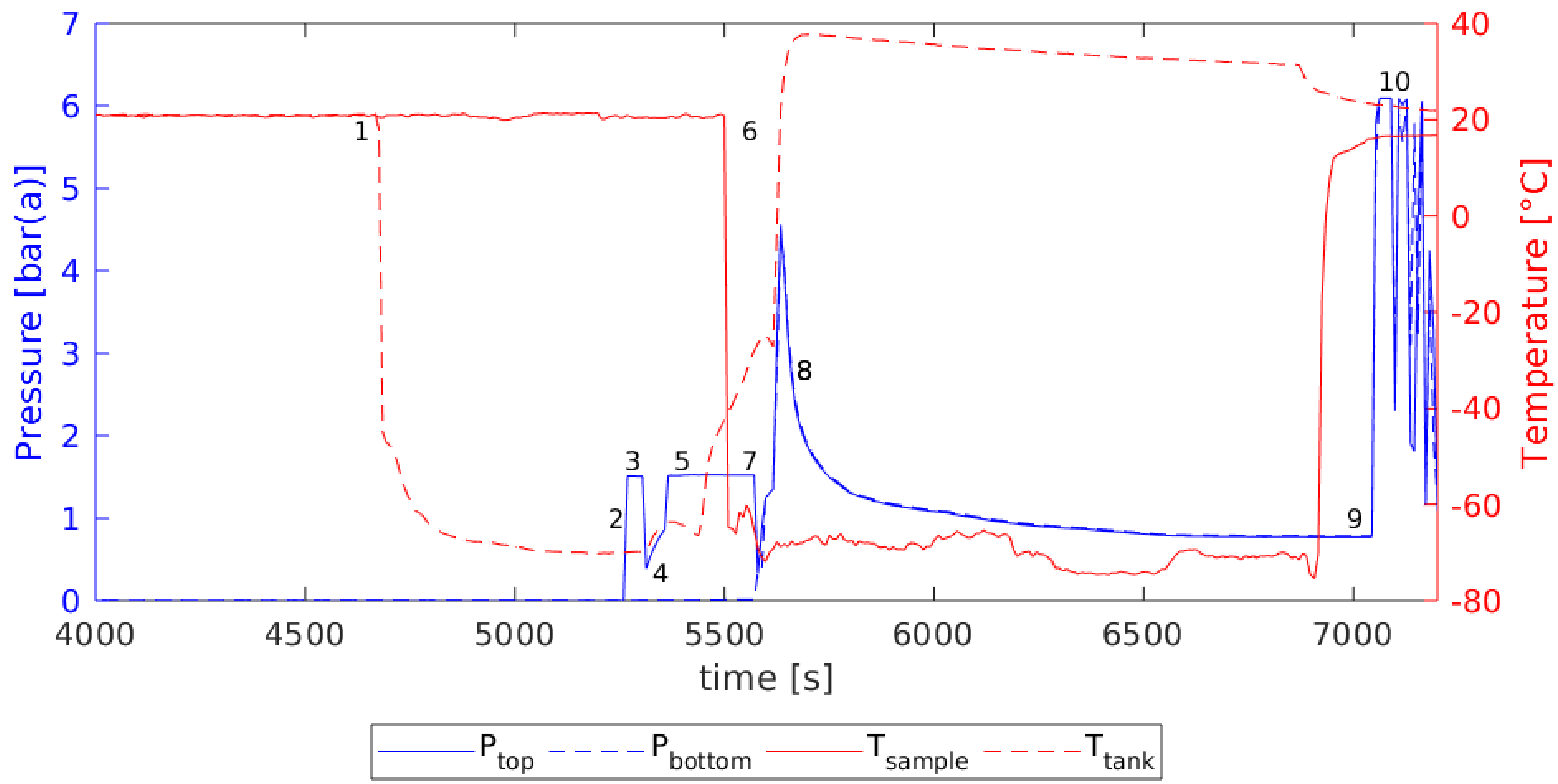
- **Sample filling**
  - **Gases**
  - All vacuum fittings and glassware are removed from the filling side.
  - Gas supplied from a tank through gas regulator at fixed inlet pressure.
  - Entegris Gatekeeper gas purifier GPU YX 70 used to reduce contaminants and increase gas purity.
  - Gas condensed in different locations using IPA/dry-ice cooling baths at -70°C.

  - A purge fill and operation in reflux mode for was performed before re-filling with fresh working fluid.



WP3 Manufacture

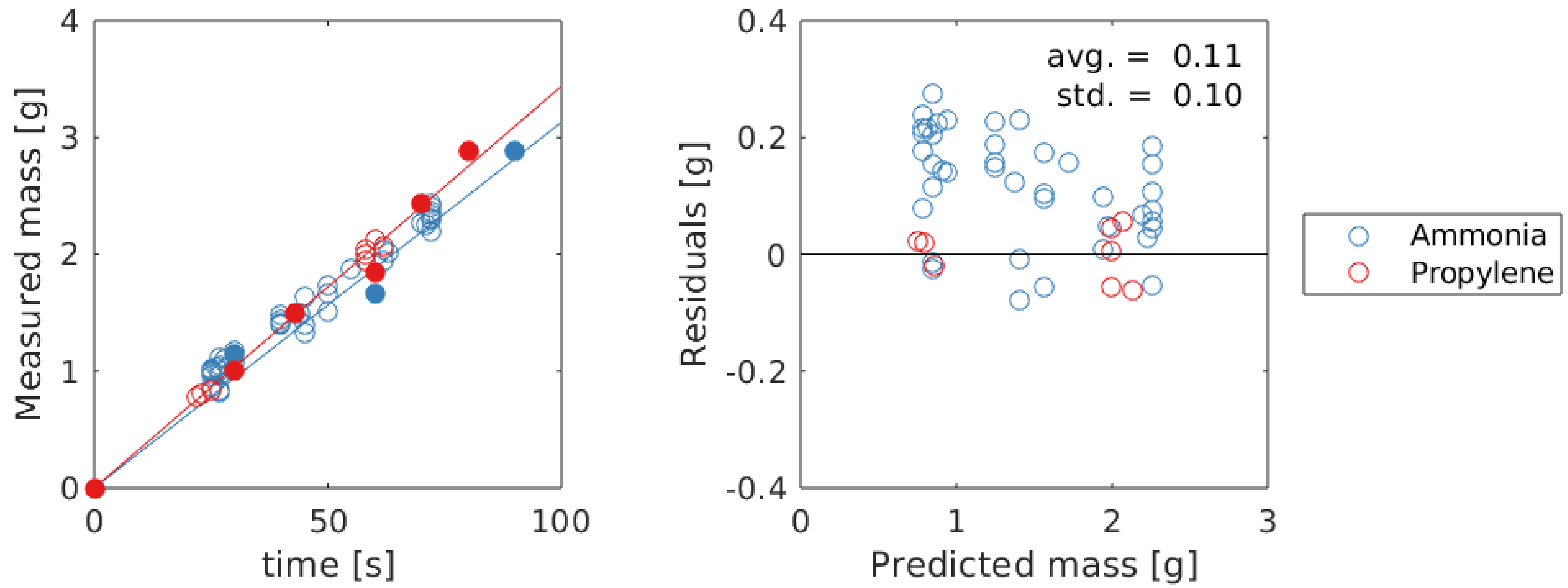
- **Sample filling**
  - **Gases**
  - The methodology for gas filling generally used is known as vapour transfer or distillation.



UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

WP3 Manufacture

- **Sample filling**
  - **Gases**
  - A calibration process is required to relate filling mass to filling time.



WP3 Manufacture

- **Sample filling**
  - **Gases**

Gas inlet + purifier + regulator (in back)

Upper and lower lines joined

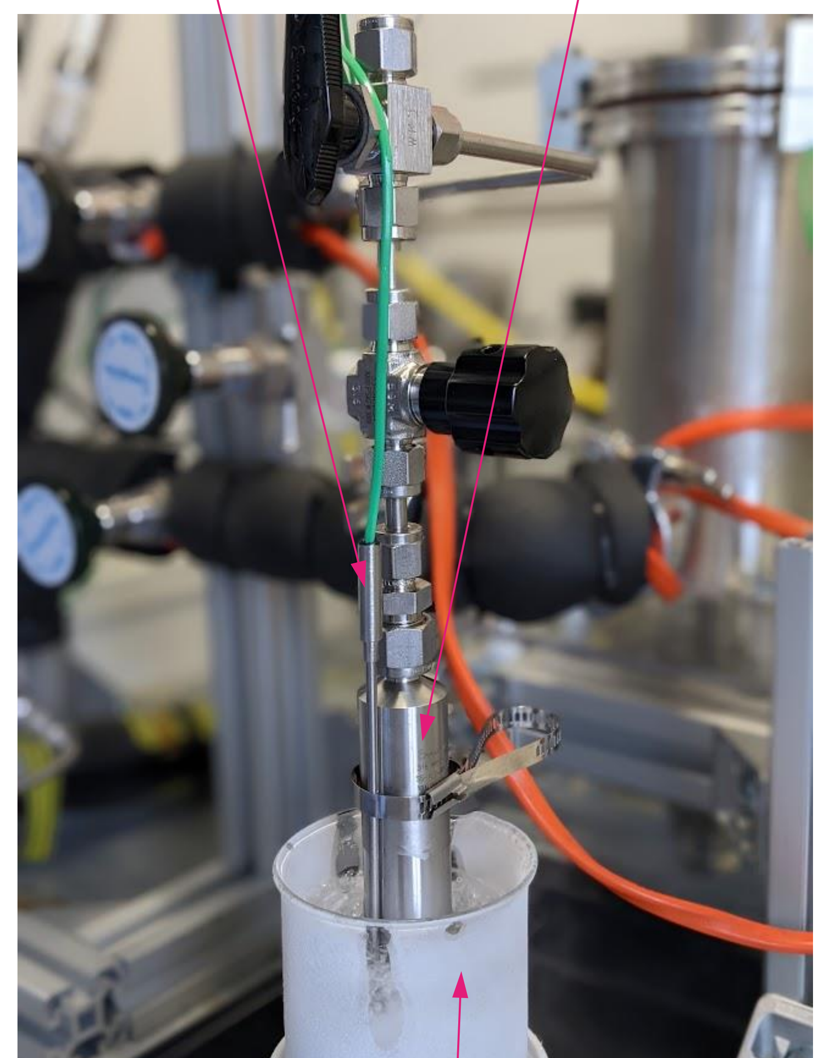
Sample

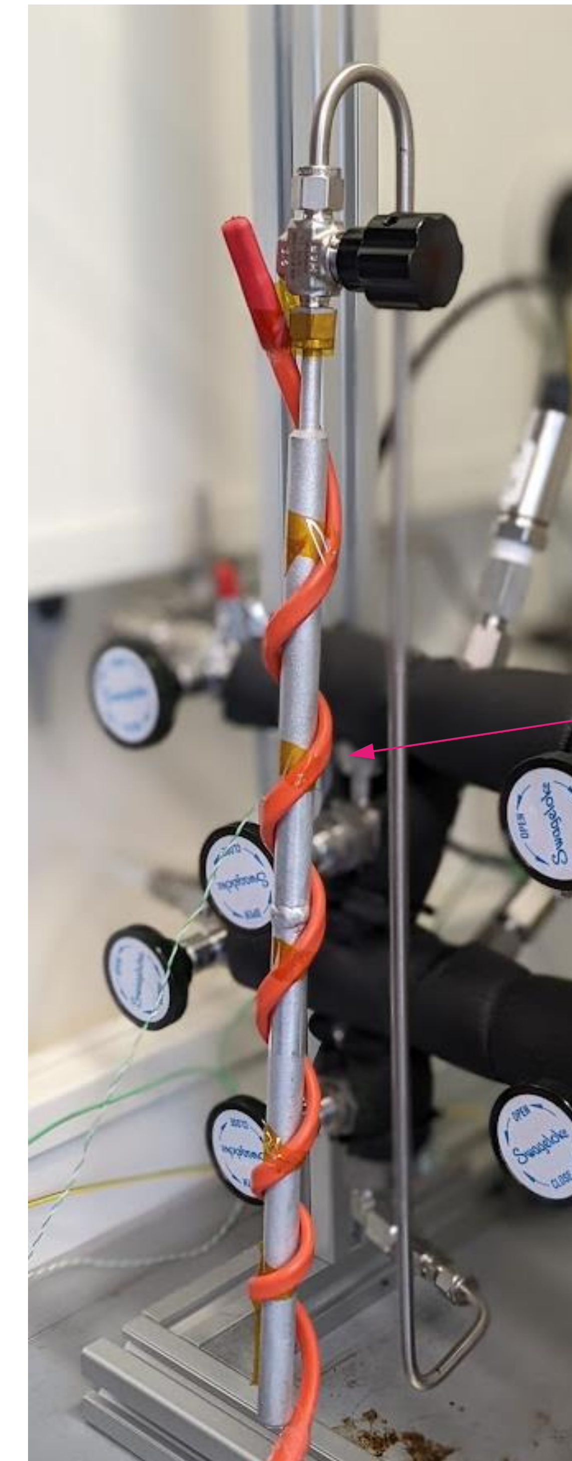
N2 purging line

Intermediate tank

WP3 Manufacture

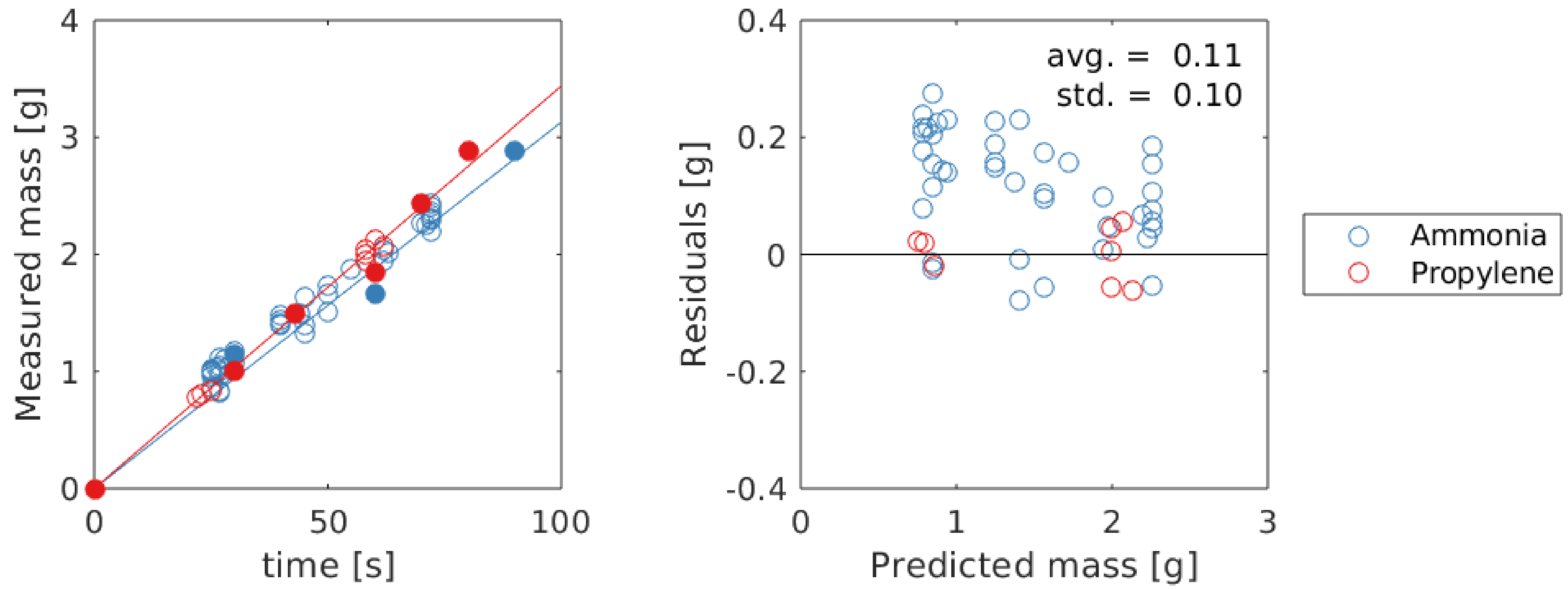
- **Sample filling**
  - **Gases**





WP3 Manufacture

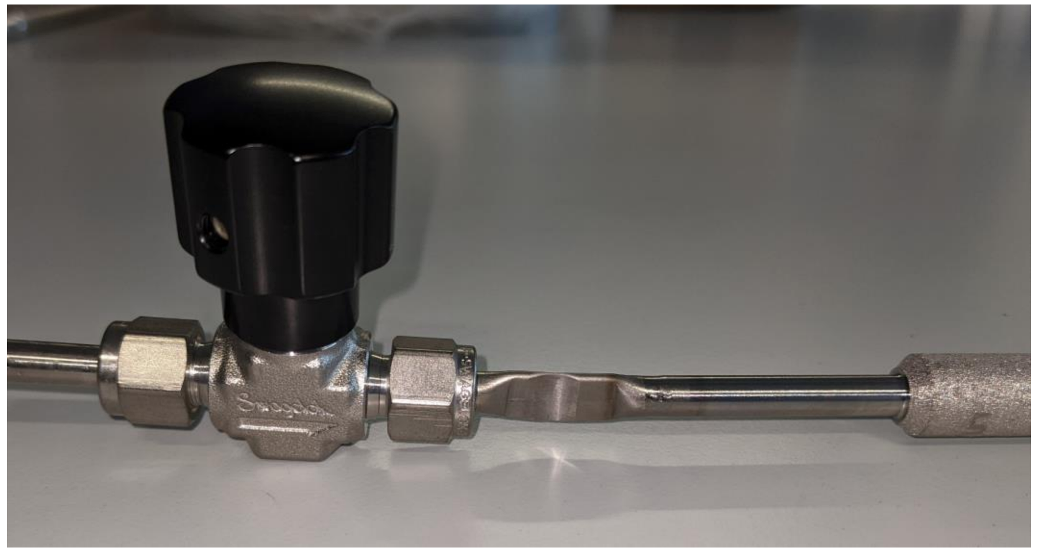
- **Sample filling**
  - **Gases**
  - The filling masses were verified by measuring the combined sample and valve mass before and after filling and after they had warmed back to ambient temperature and dried.

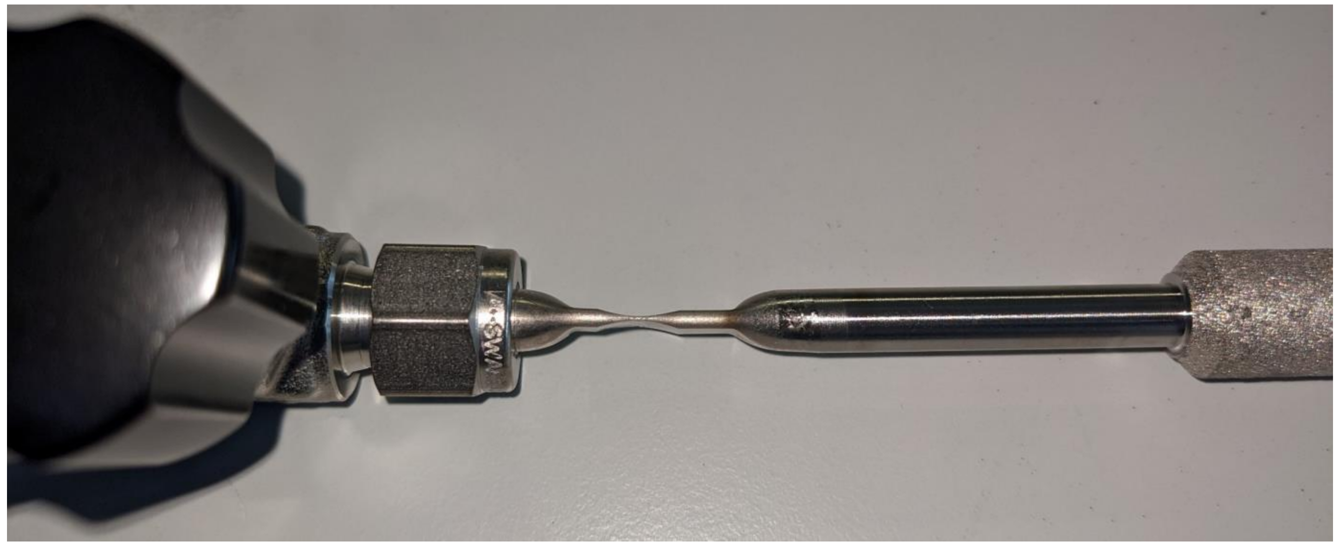


  - In general, the samples were slightly overfilled (average of 0.11 g) due to delays in either manually starting the timer or closing the tank valve after the elapsed time.

WP3 Manufacture

- **Sample sealing**
  - 3 identical samples for each fluid metal combination => 1 sample with valve + 2 crimp sealed.
  - Problems with Ti CP Grade 2 tubing crimping on samples, so valves retained in all cases.





  - Later testing of Ti CP Grade 2 tubing with 2 mm OD passed leak test, so may be a better option in future.

WP3 Manufacture

- **Sample sealing**
  - For high pressure fluids (i.e., ammonia and propylene), an additional TIG weld across the cut-off section was used to ensure sealing.
  - No filler wire is added, the crimped end is remelted to form a seal.

SS316L ALM

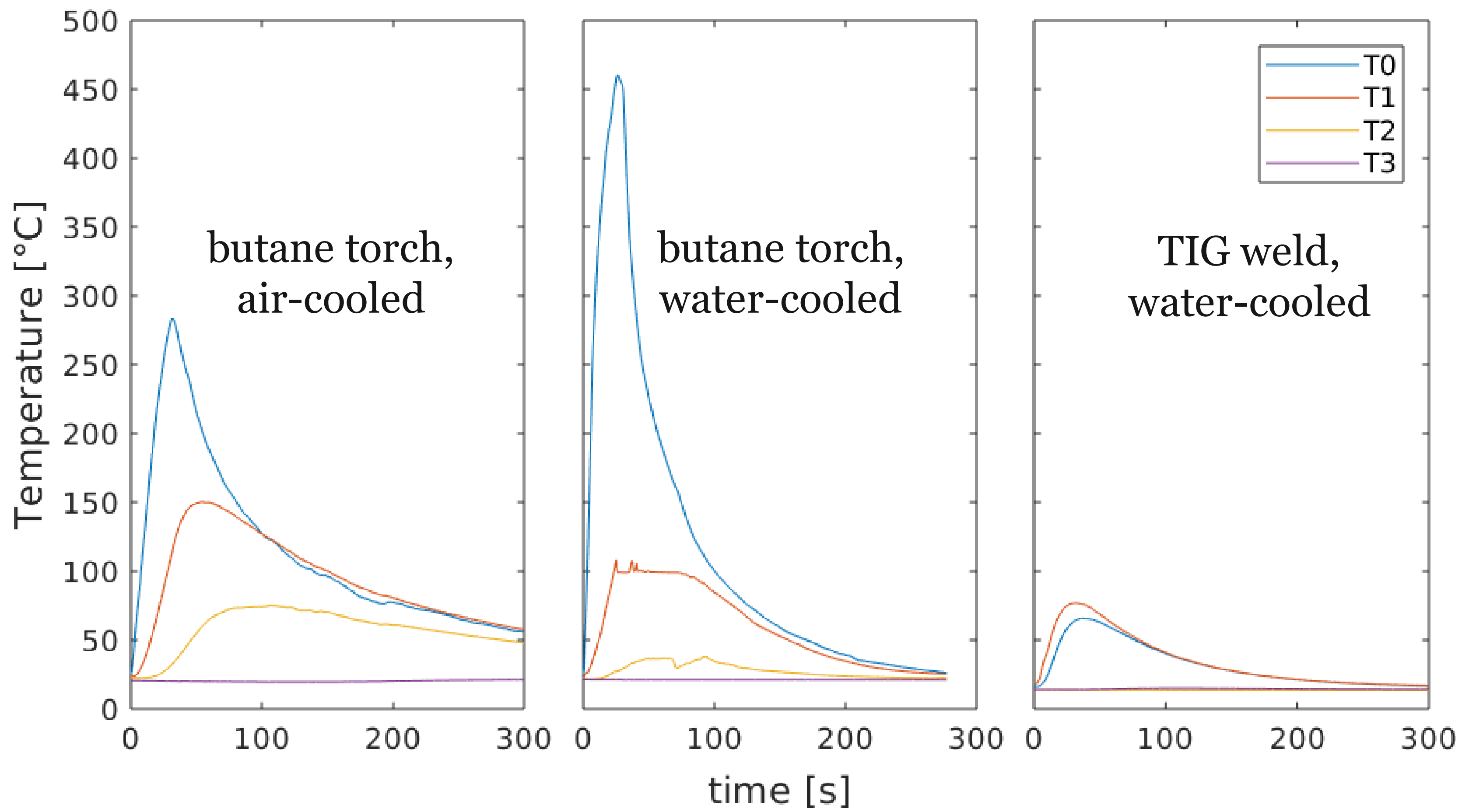
AlSi7Mg

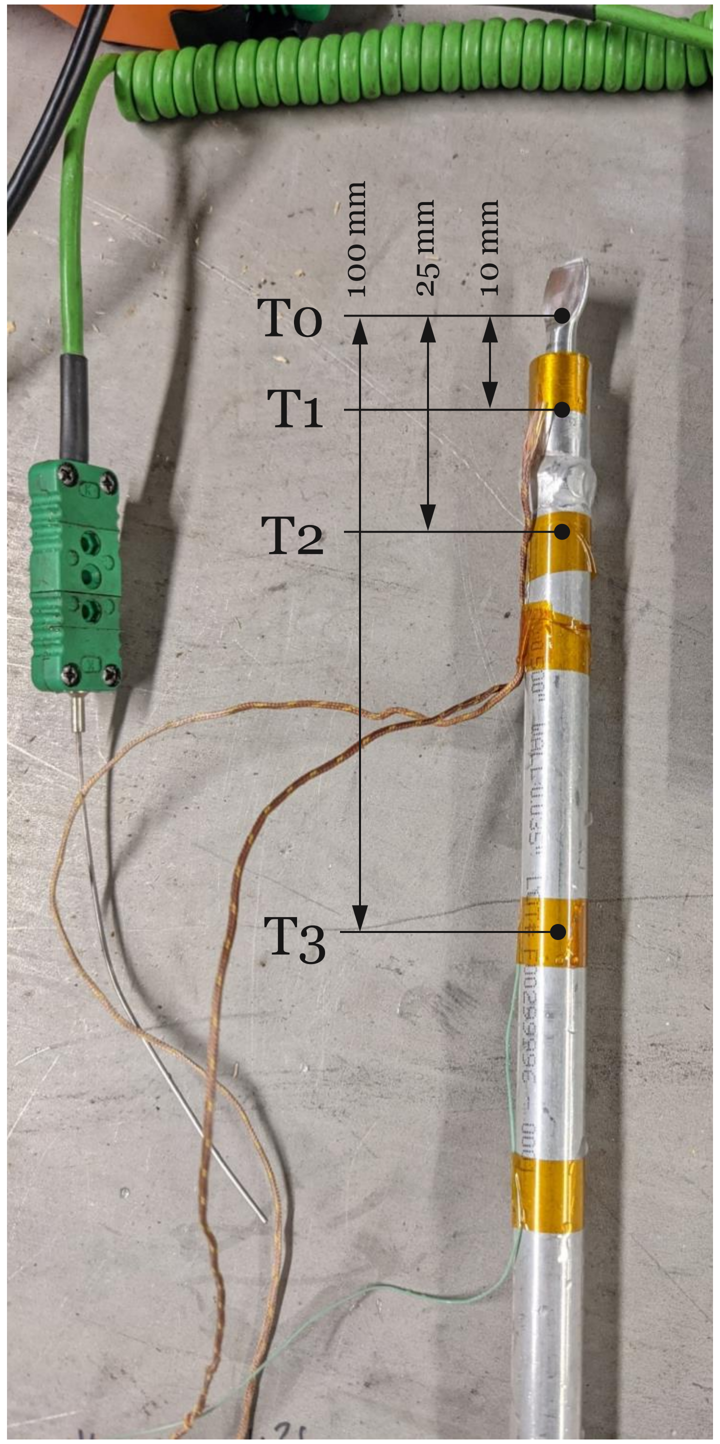
  - End weld sealing was also performed on samples with ethylene glycol due to the later detection of some leaks on other liquid samples

UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

WP3 Manufacture

- **Sample sealing**
  - Trials to measure temperature profile along the tube during welding to minimise vapour pressure of container working fluid.





  - Each sample was set up in turn in the welding rig and water bath, clamp was place on the crimped section, valve was removed, and the welding seal was performed.

WP3 Manufacture

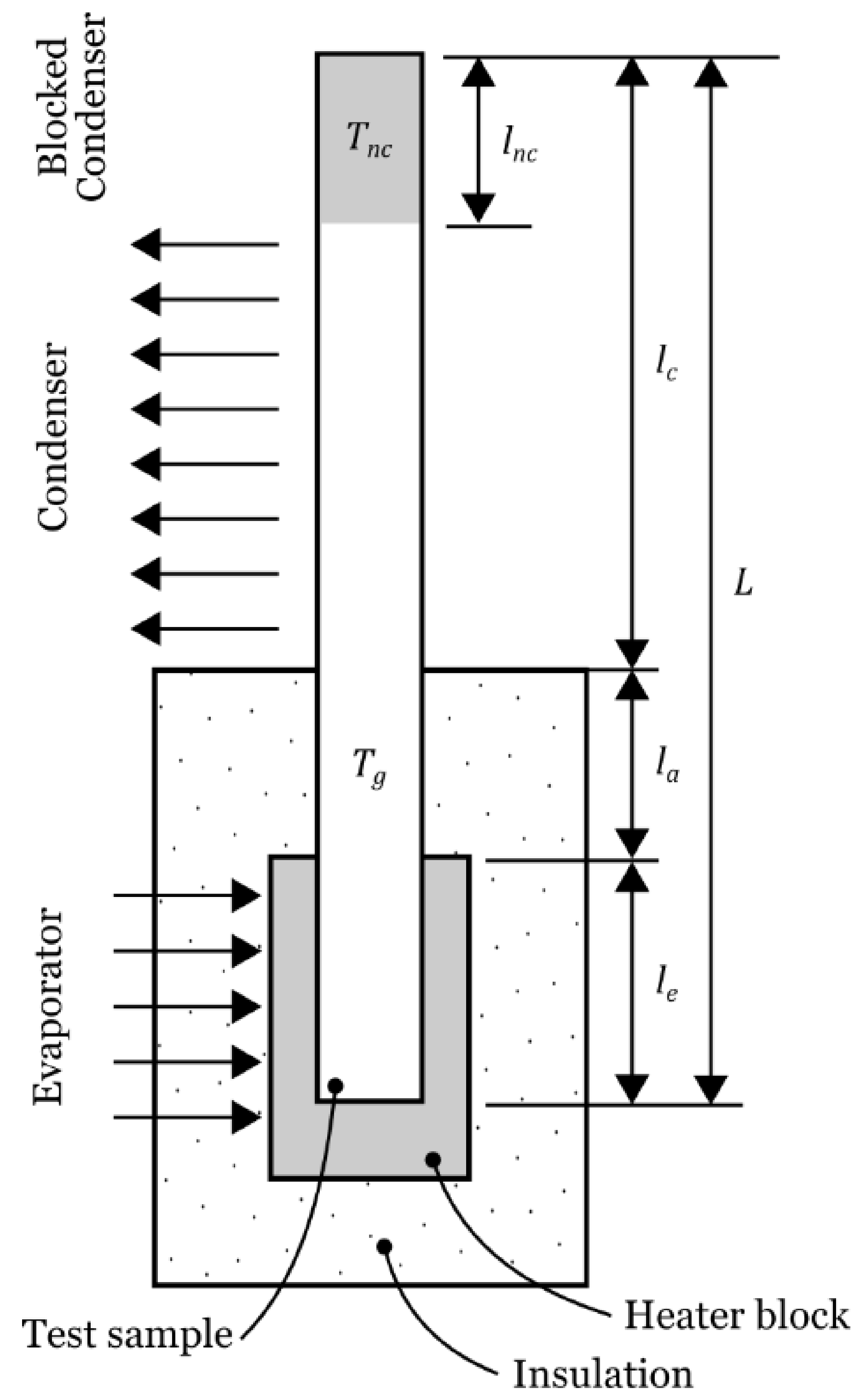
- **Sample sealing**
  - Weld success verified with red litmus paper.
  - Ammonia has pH 11-13 and will turn paper blue.

WP3 Manufacture

- **Gas Plug Test Definition**
  - The blockage length of NCG as a function of the operating temperature, tube design and working fluid purity can be estimated from:

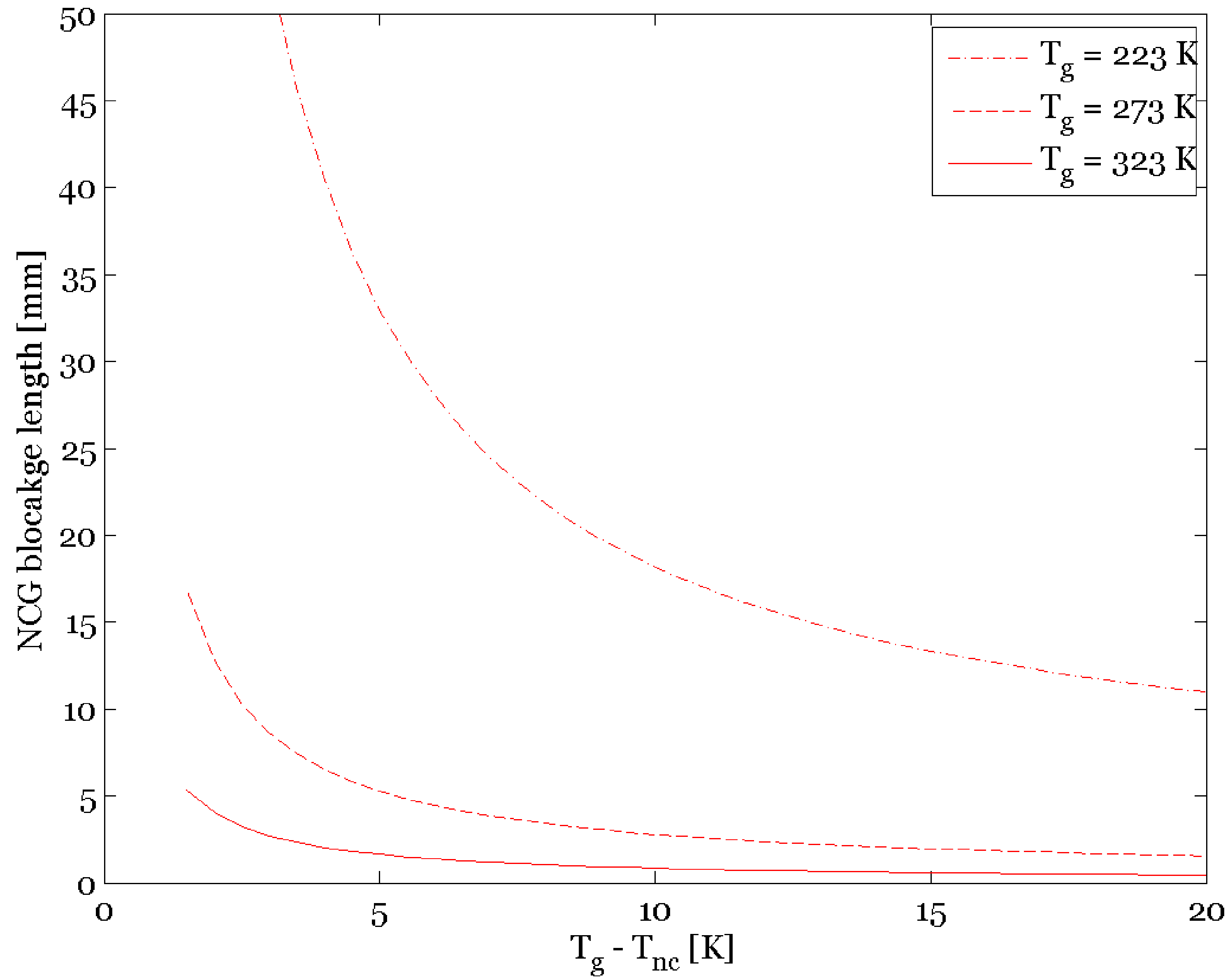
$$\frac{l_{nc}}{L} = \frac{f n_l R T_{nc}}{L A_g \left[P_g(T_g) - P_g(T_{nc}) \right]}$$

where f is fluid purity, n_l is the number of moles of working fluid, R is the gas constant, A_g is the vapour space cross section area, and P is pressure.



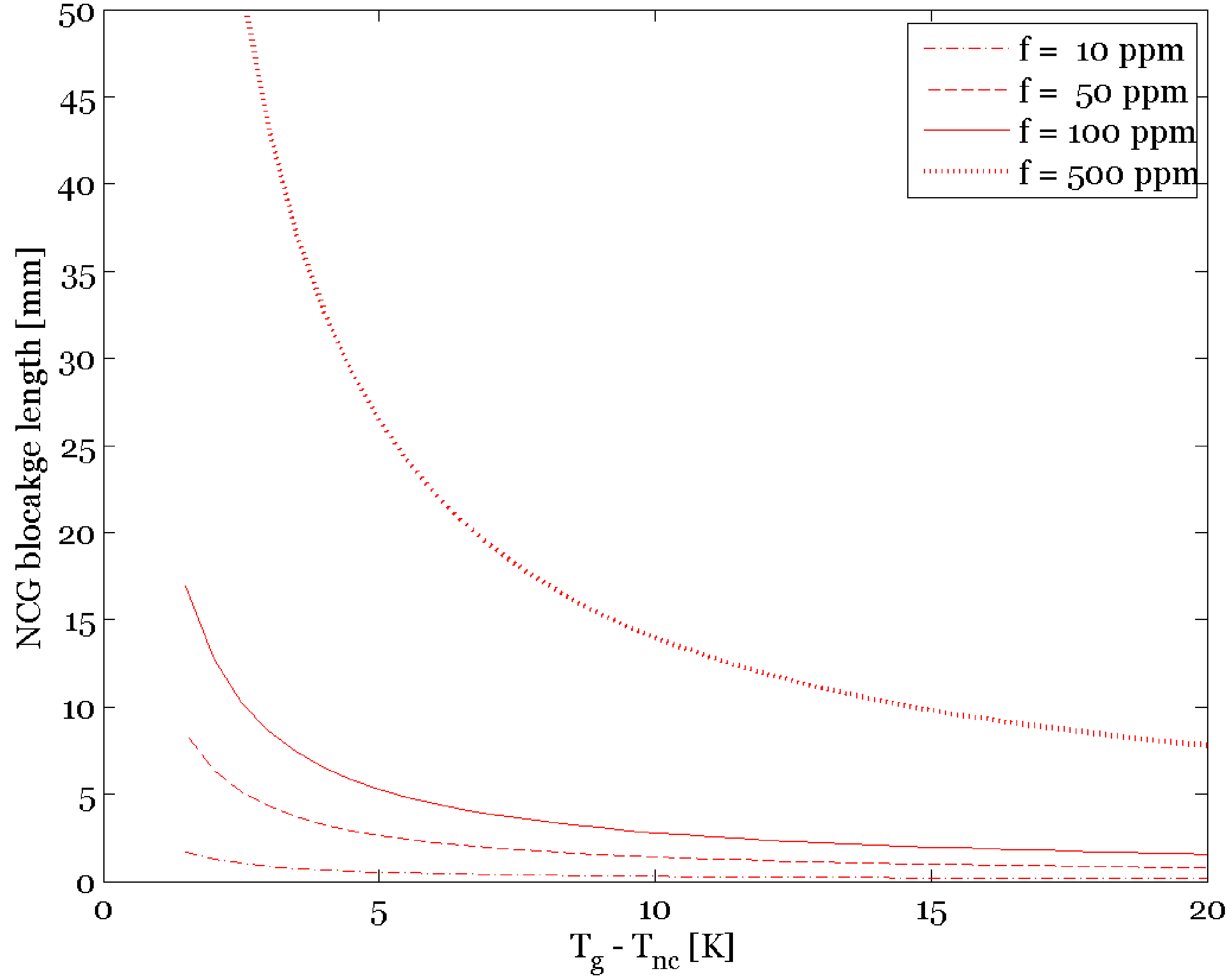
WP3 Manufacture

- **Gas Plug Test Definition**
  - *Case 1* : Effect of operating temperature for ammonia thermosyphon (OD = 12.7 mm, wall = 0.9 mm, *L* = 400 mm, ***f* = 100 ppm**, filling volume as listed previously)



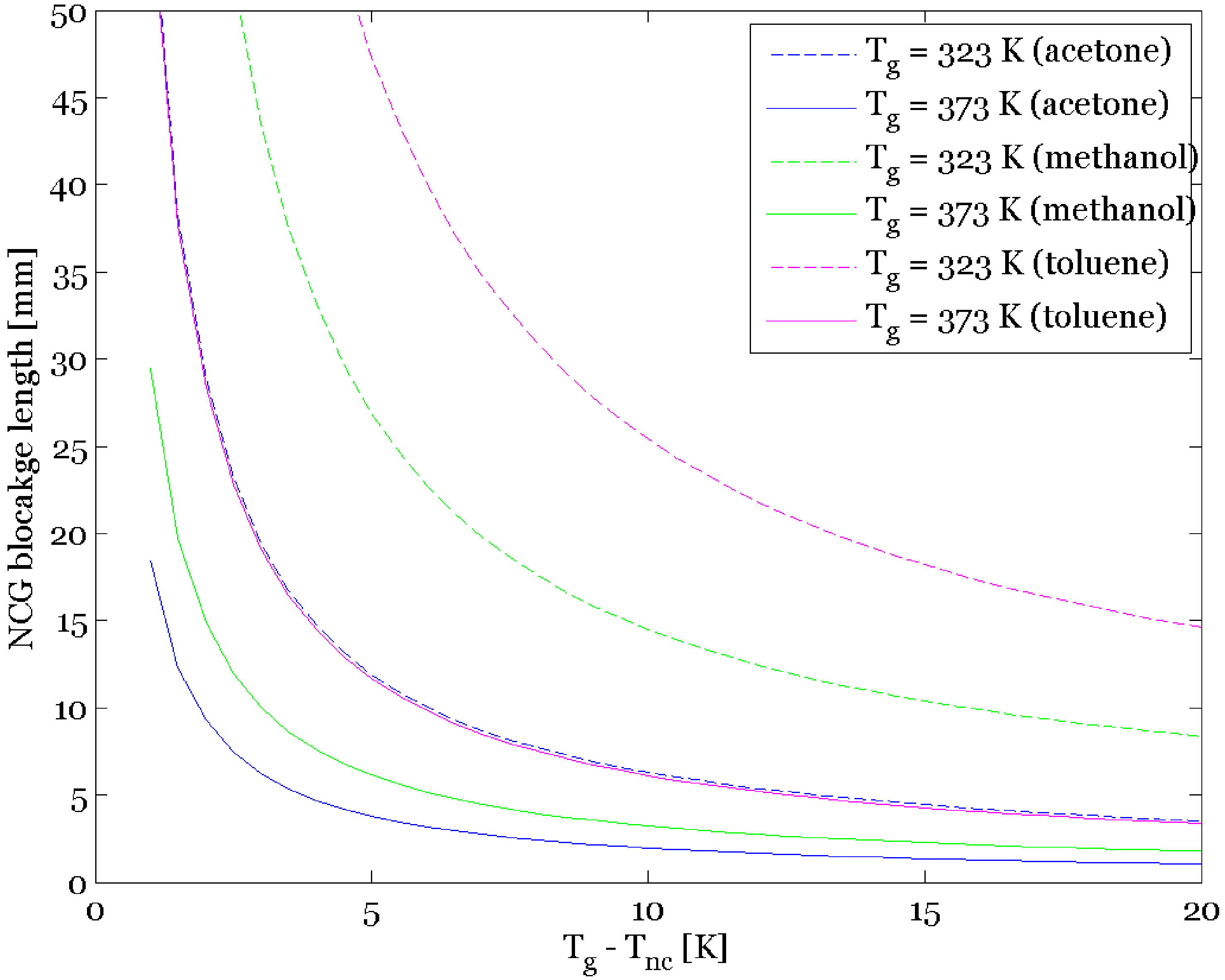
WP3 Manufacture

- **Gas Plug Test Definition**
  - *Case 2*: Effect of fluid purity for aluminium-ammonia thermosyphon (OD = 12.7 mm, wall = 0.9 mm, *L* = 400 mm, $\boldsymbol{T_g = 273\ K}$, filling volume as listed previously)



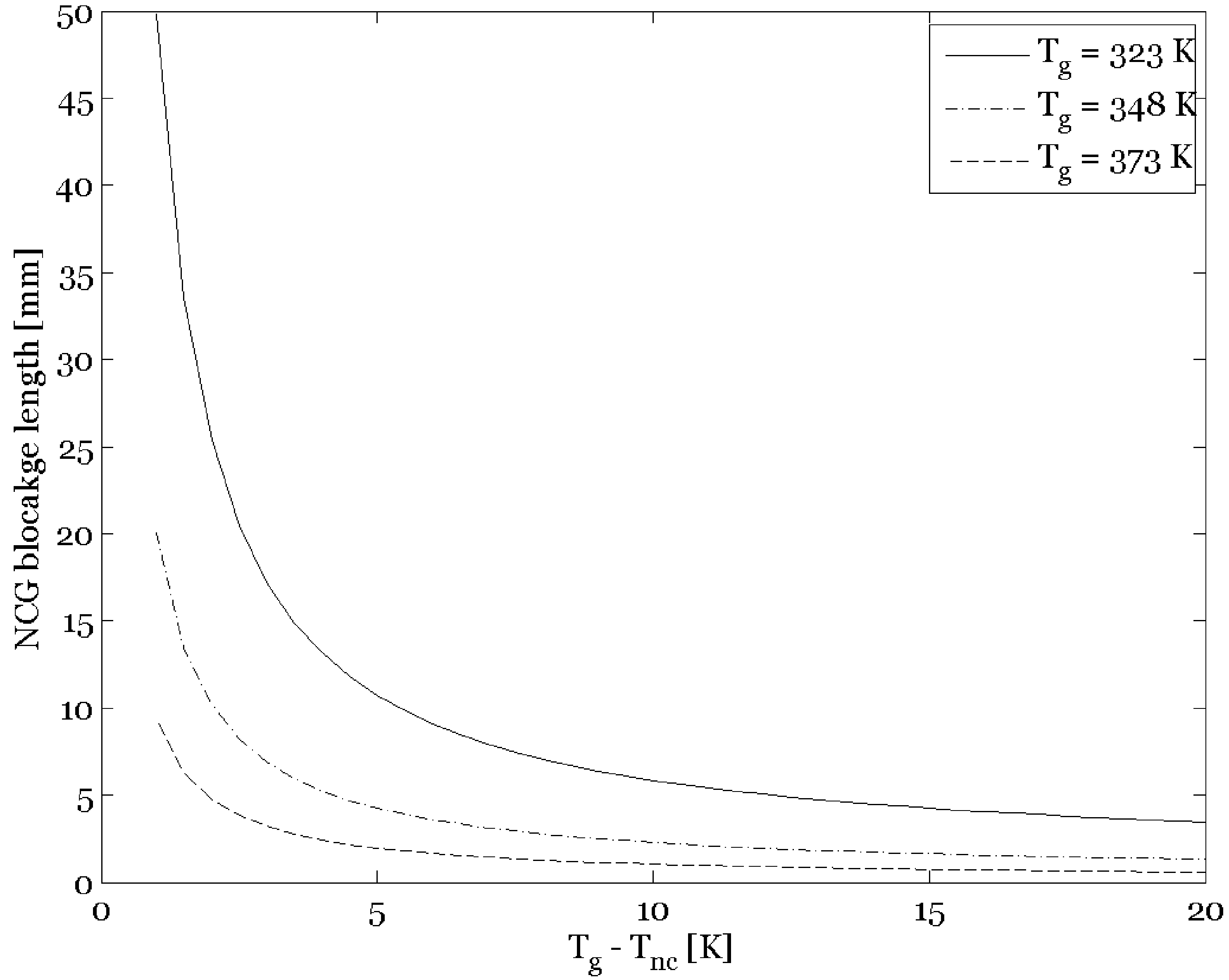
WP3 Manufacture

- **Gas Plug Test Definition**
  - *Case 3*: Effect of operating temperature for aluminium-acetone, methanol and toluene thermosyphons (OD = 12.7 mm, wall = 0.9 mm, L = 400 mm, $\boldsymbol{f}$ **= 100 ppm**, filling volume as listed previously)



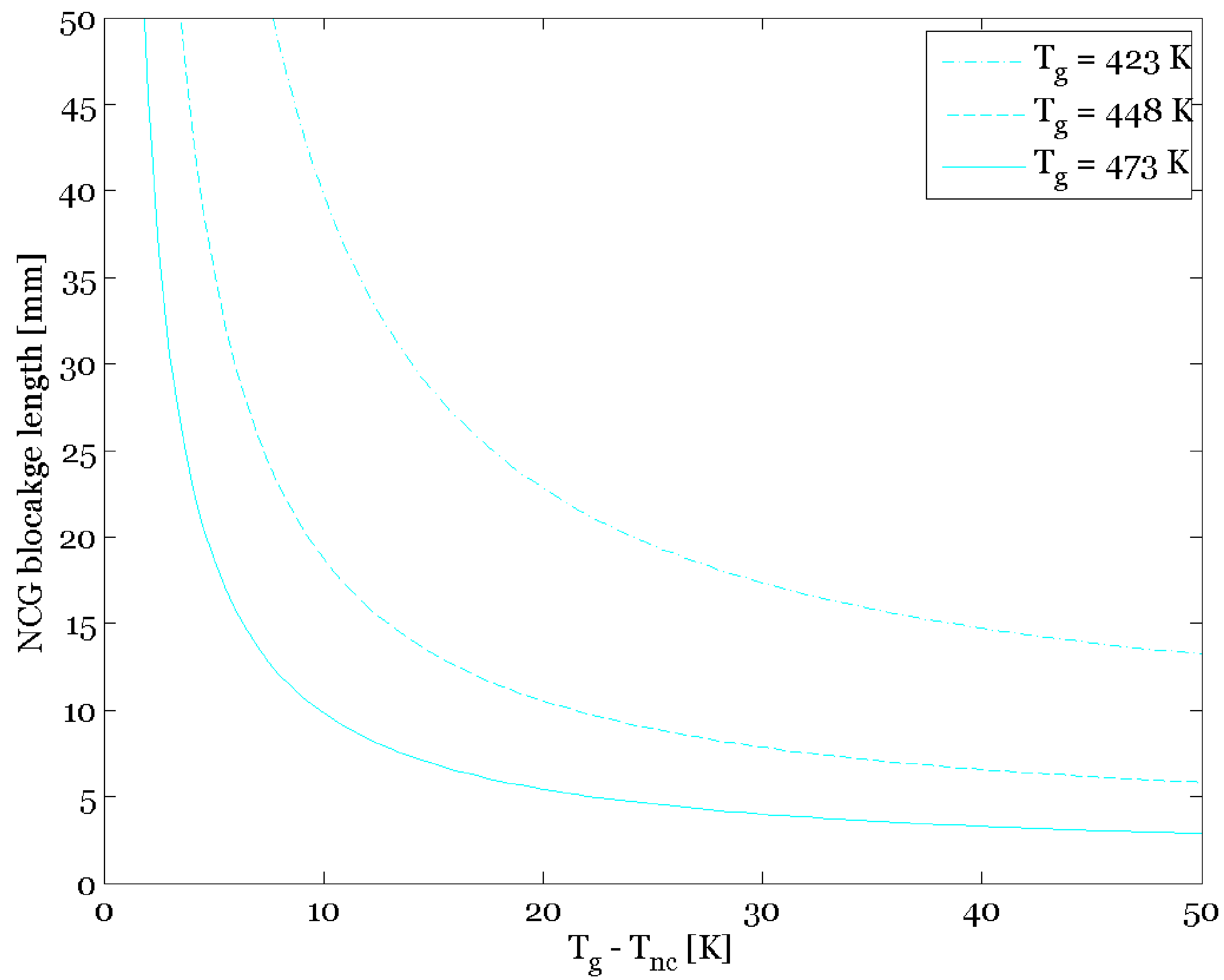
WP3 Manufacture

- **Gas Plug Test Definition**
  - *Case 4*: Effect of operating temperature for stainless-steel-water thermosyphon (OD = 12.7 mm, wall = 0.9 mm, *L* = 180 mm, ***f* = 10 ppm**, filling volume as listed previously)



WP3 Manufacture

- **Gas Plug Test Definition**
  - *Case 5*: Effect of operating temperature for aluminium-ethylene glycol thermosyphon (OD = 12.7 mm, wall = 0.9 mm, *L* = 400 mm, ***f* = 100 ppm**, filling volume as listed previously)



WP3 Manufacture

- **Gas Plug Test Definition**
  - A similar analysis can be performed for estimating the effect of the number of free gas molecules remaining in the sample after vacuum evacuation during the filling process.
  - For vacuum of 10^{-1} mbar => equivalent to f = 0.9 ppm and l_{nc} = 0.5 mm.

WP3 Manufacture

- **Gas Plug Test Definition**
  - Four sets of different temperature boundary conditions:

Description	Operating condition	
Condenser		
Environ. chamber temperature	293 K	
Environ. chamber humidity	55 % RH	
Evaporator	Measurement set point temperature [K]	Operating set point temperature [K]
Ammonia	298	323
Acetone	373	373
Methanol	373	373
Toluene	373	373
Propylene	298	323
Ethylene glycol	423	423
Water	348	348

Group 2: Acetone, Methanol, Toluene
Group 1: Water
Group 4: Ammonia, Propylene
Group 3: Ethylene glycol

  - Thermocouples at 10 and 30 mm from condenser, and at top of evaporator for each sample.

WP3 Manufacture

- **Gas Plug Test Manufacture**

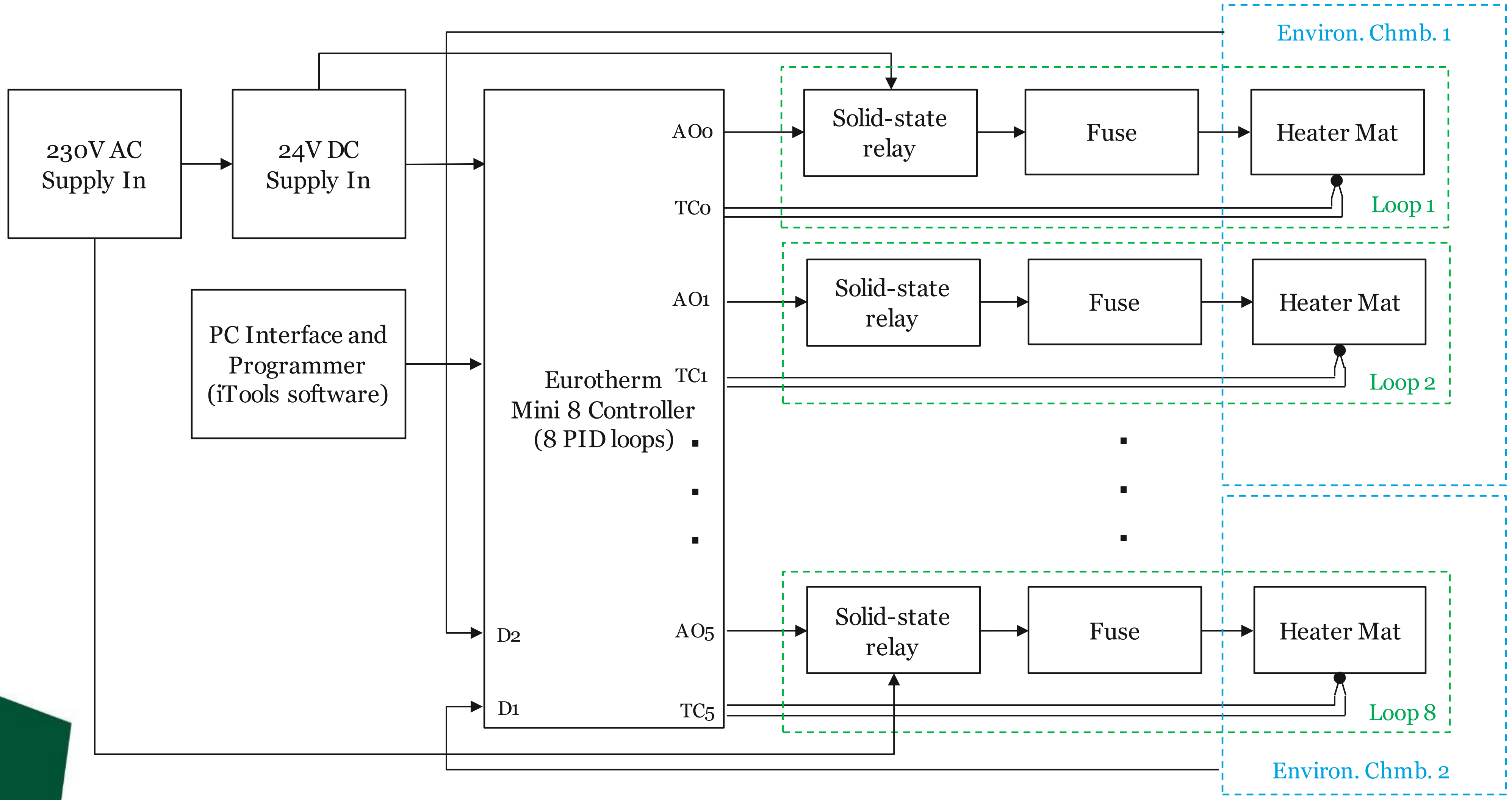
Group	Total no. of samples	Total no. of short samples	Total no. of long samples	Total no. of irregular samples
		SS316L, Ti6Al4V, Invar	AlSi10Mg, AlSi7Mg	Al6061, bimetallic, ScouP
1 : Water	**6**	6	--	--
2 : Acetone, Methanol, Toluene	**35**	20	12	3
3 : Ethylene glycol	**15**	6	6	3
4 : Ammonia and Propylene	**41**	14	12	15

- For short and long samples => aluminium heater blocks
- For irregular samples => oil bath

UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH Bernal Institute

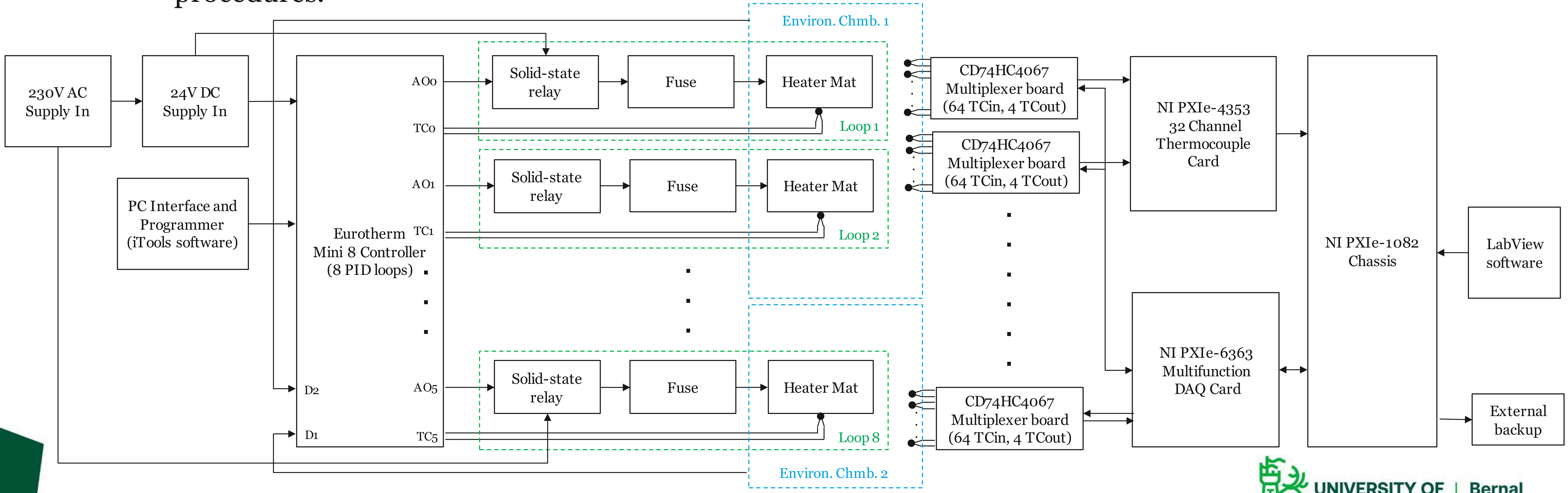
WP3 Manufacture

- **Gas Plug Test Manufacture**
  - Omega KHLVA-204/10-P 80 W Heater mat attached to aluminium block and controlled by a corresponding PID controller located outside chamber.
  - Block insulated to reduce heat loss.



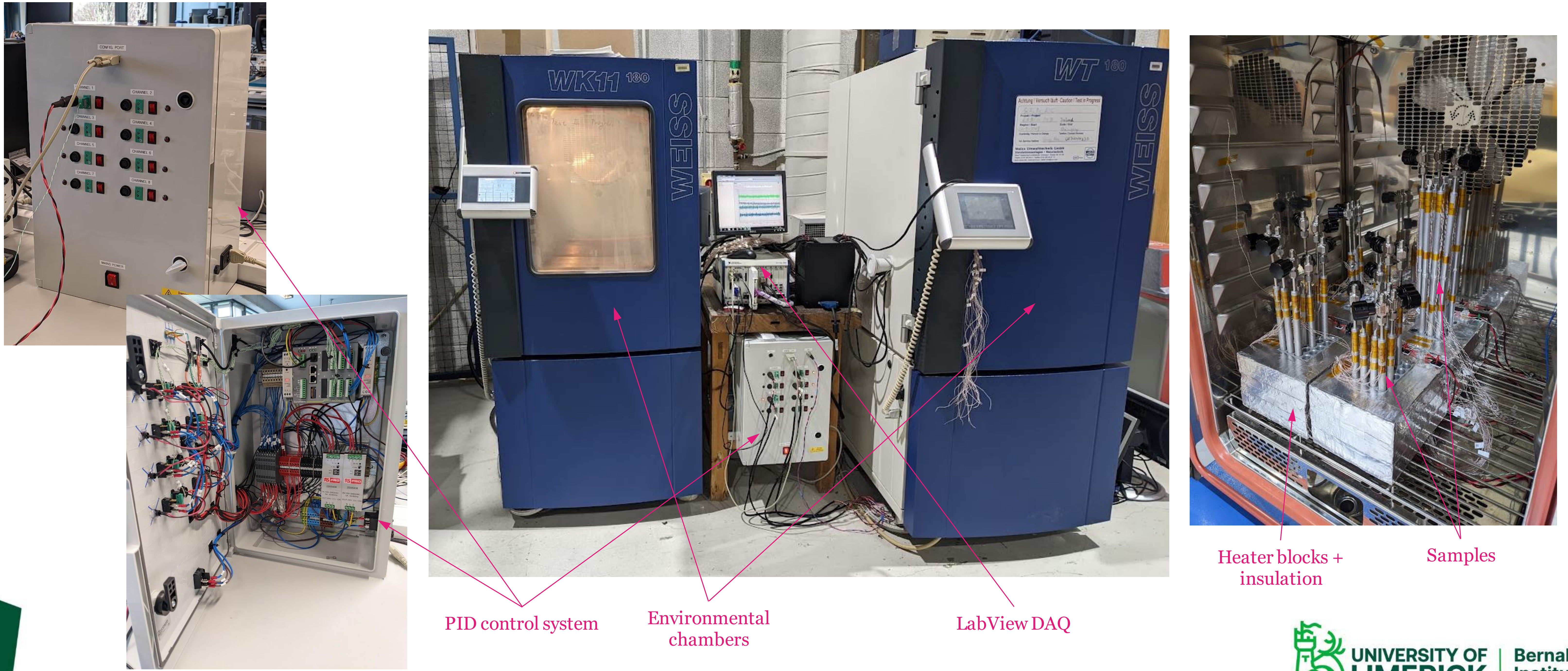
WP3 Manufacture

- **Gas Plug Test Manufacture**
  - For temperature profile and monitoring measurements, >**300** T-type thermocouples.
  - NI LabView DAQ system + multiplexers to record all temperature measurements.
  - All thermocouples calibrated in recirculating heated water bath (stability of ± 0.05°C) following standard procedures.



WP3 Manufacture

- **Gas Plug Test Manufacture**



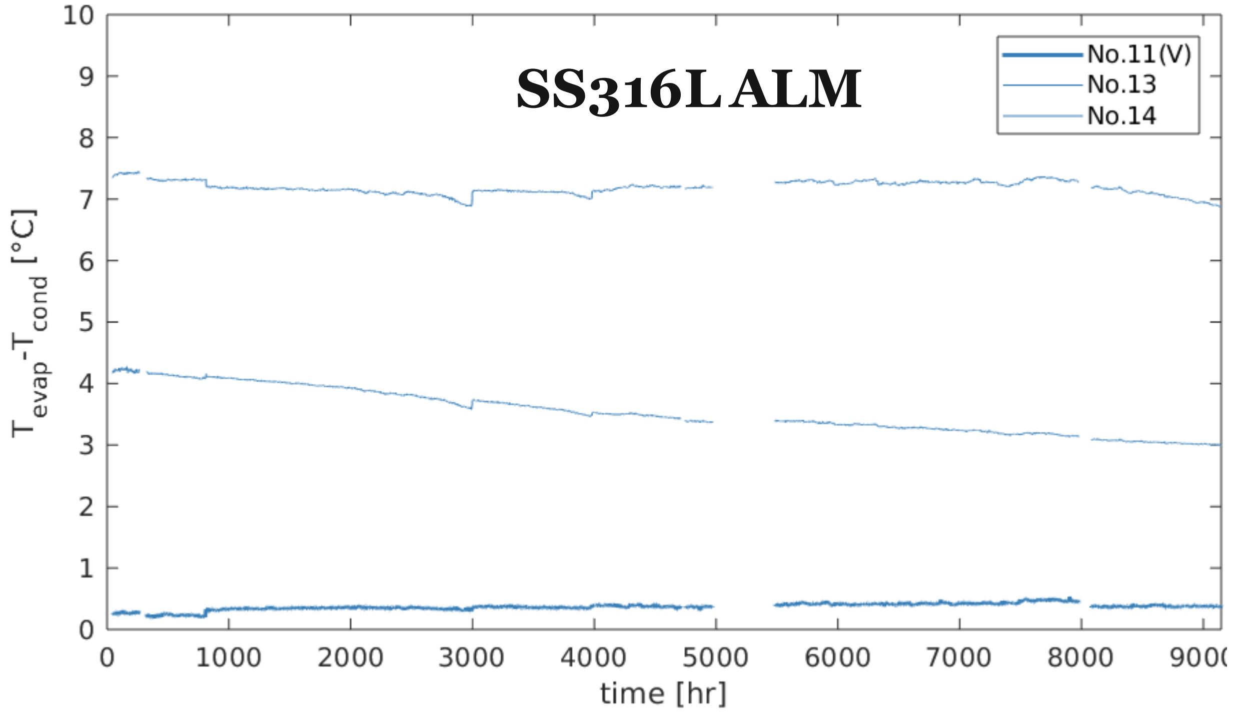
UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

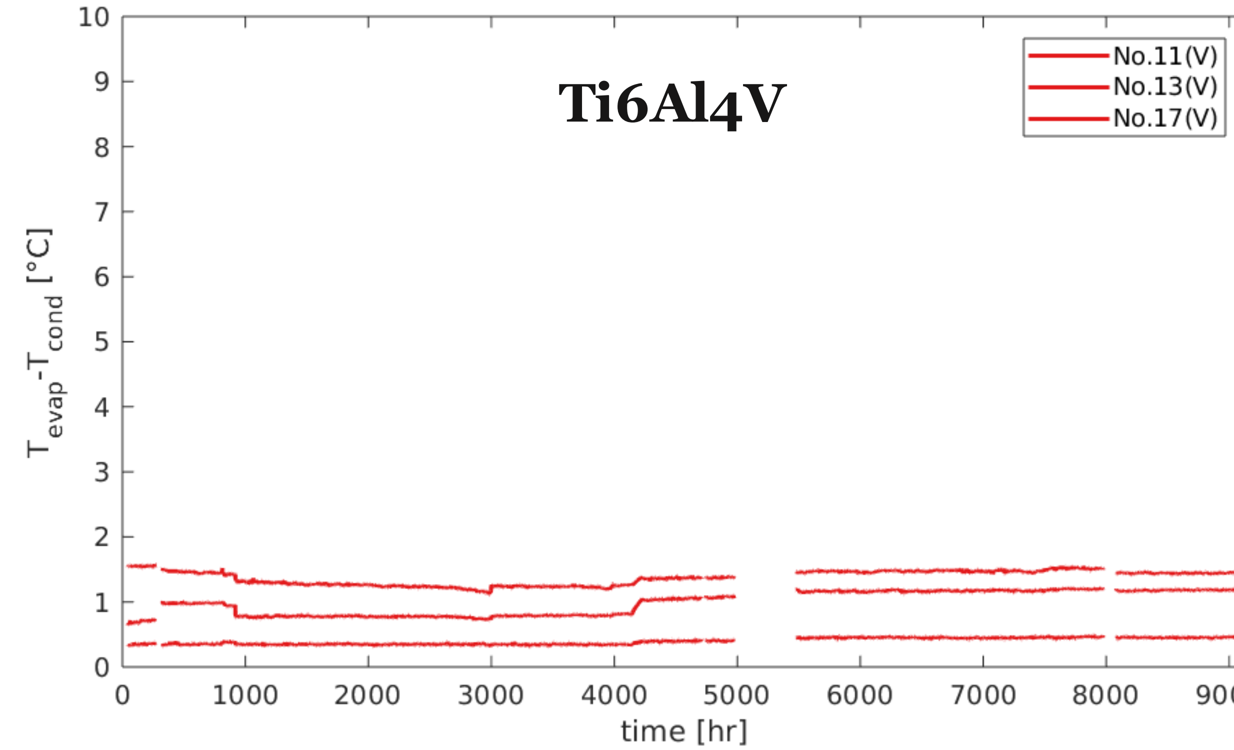
WP4 Characterisation

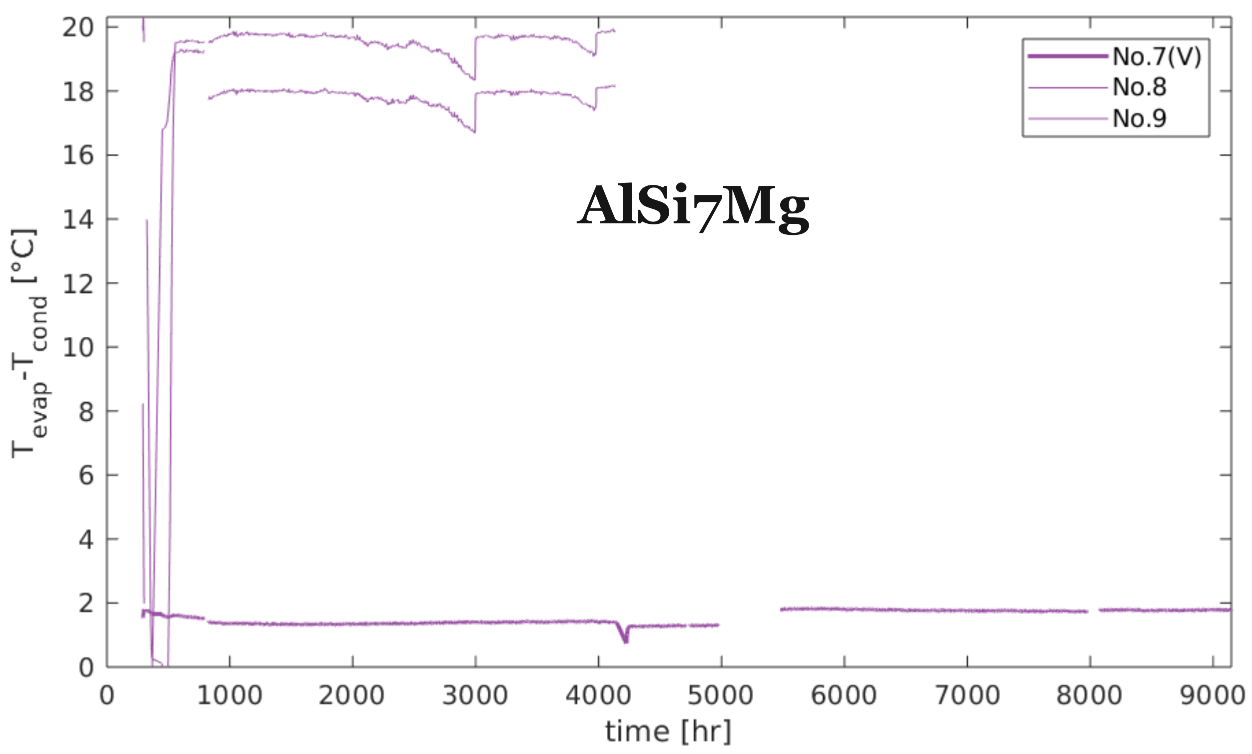
- **Gas Plug Test**
  - For liquids, started April 2022
  - For gases, started November 2022
  - For SCouP, started March 2023
- **Corrosion analysis** for selected samples based on Gas Plug performance:
  - Gas Chromatography
  - Sample sectioning
  - X-ray photoelectron spectroscopy (XPS)
  - SEM/EDX
- **Wettability characterisation of ALM materials**

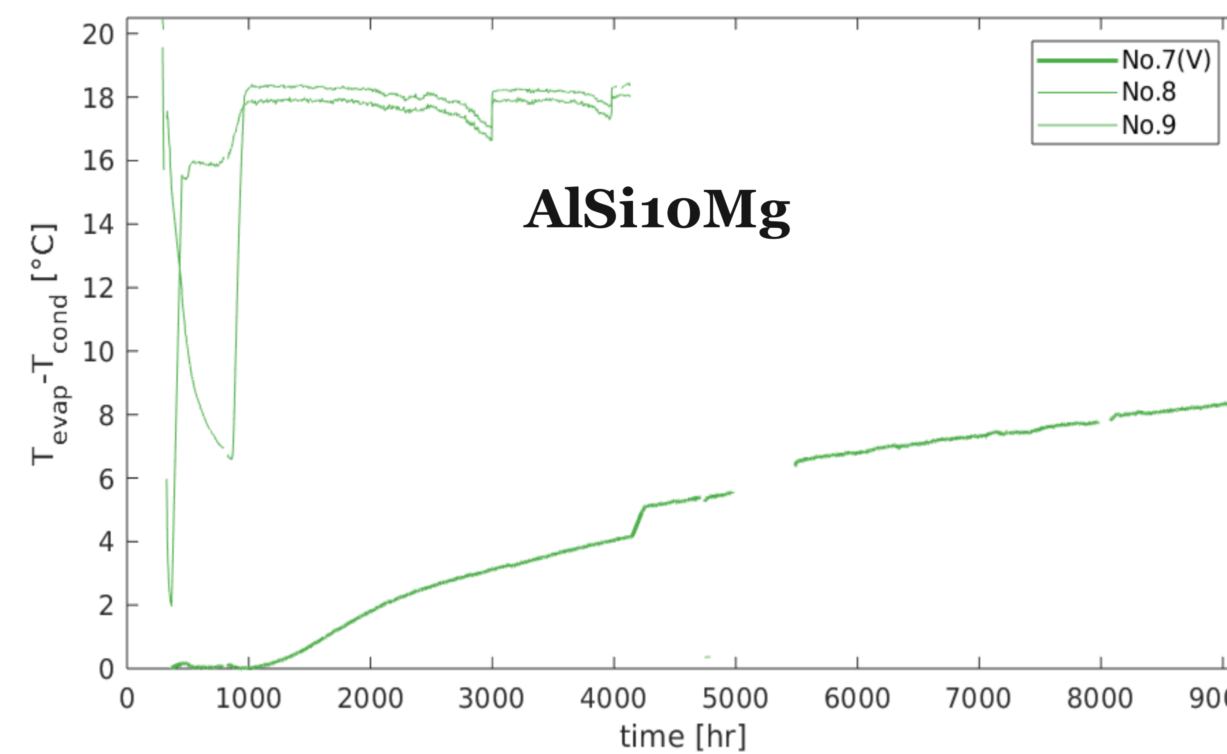
WP4 Characterisation

- **Gas Plug Test - Acetone**









WP4 Characterisation

- **Gas Plug Test - Acetone**
  - AlSi7Mg and AlSi10Mg removed from heating block and re-weighed:

Sample No.	Mass of fluid fill [g]	Mass after filling [g]	Mass after 4000 hr [g]	dMass [g]
AlSi7Mg 8	2.96	39.41	36.50	2.91
AlSi7Mg 9	3.09	40.43	37.44	2.99
AlSi10Mg 8	3.15	41.40	38.47	2.93
AlSi10Mg 9	3.03	41.55	38.61	2.94

  - Indicates leak through crimp in all cases.
  - Visible "orange" leak point on crimps.

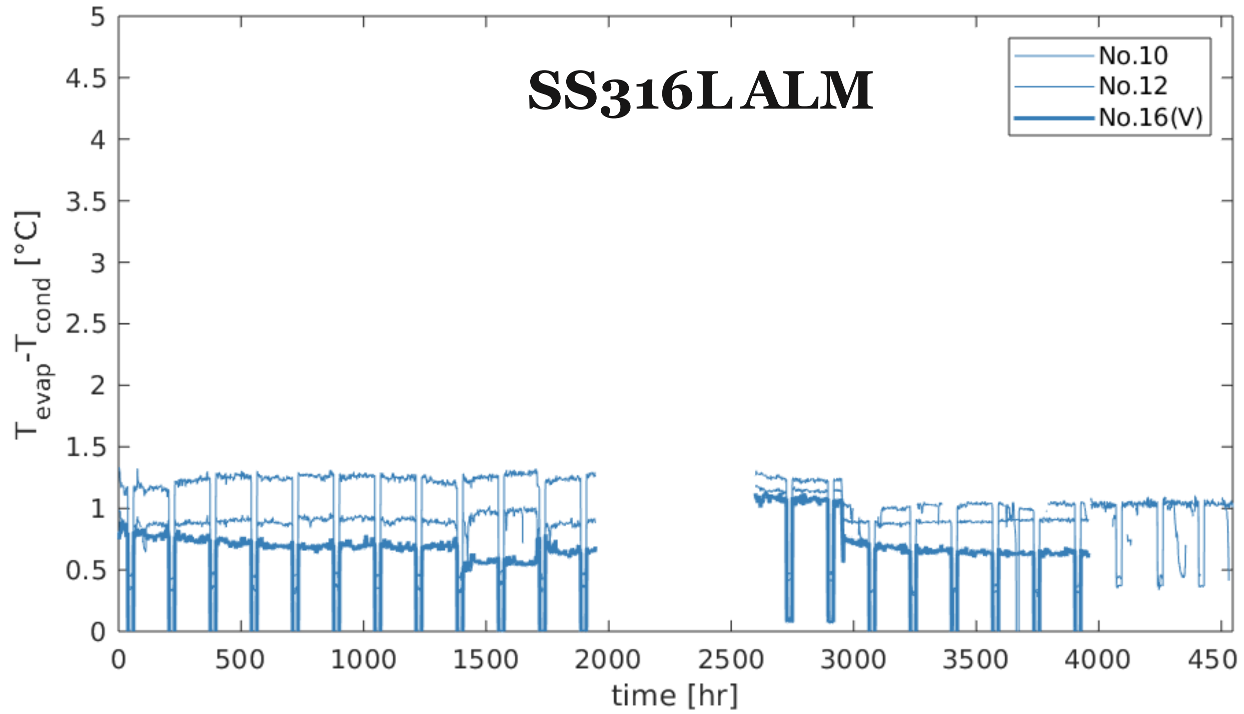
  - *Note:* Empty reference samples place in Gas Plug Test to indicate leaks or heat transfer by conduction along sample only.
    - SS316L ΔT ≈ 25°C
    - Aluminium ΔT ≈ 23C

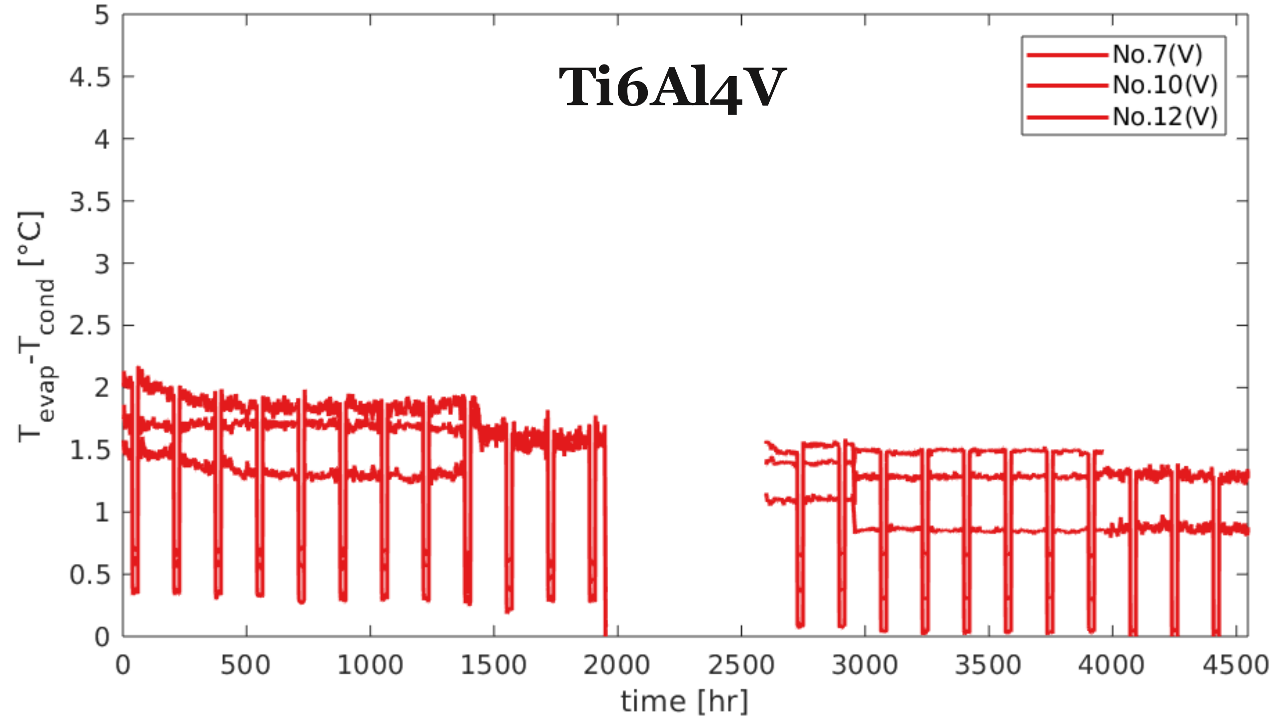
AlSi10Mg 8

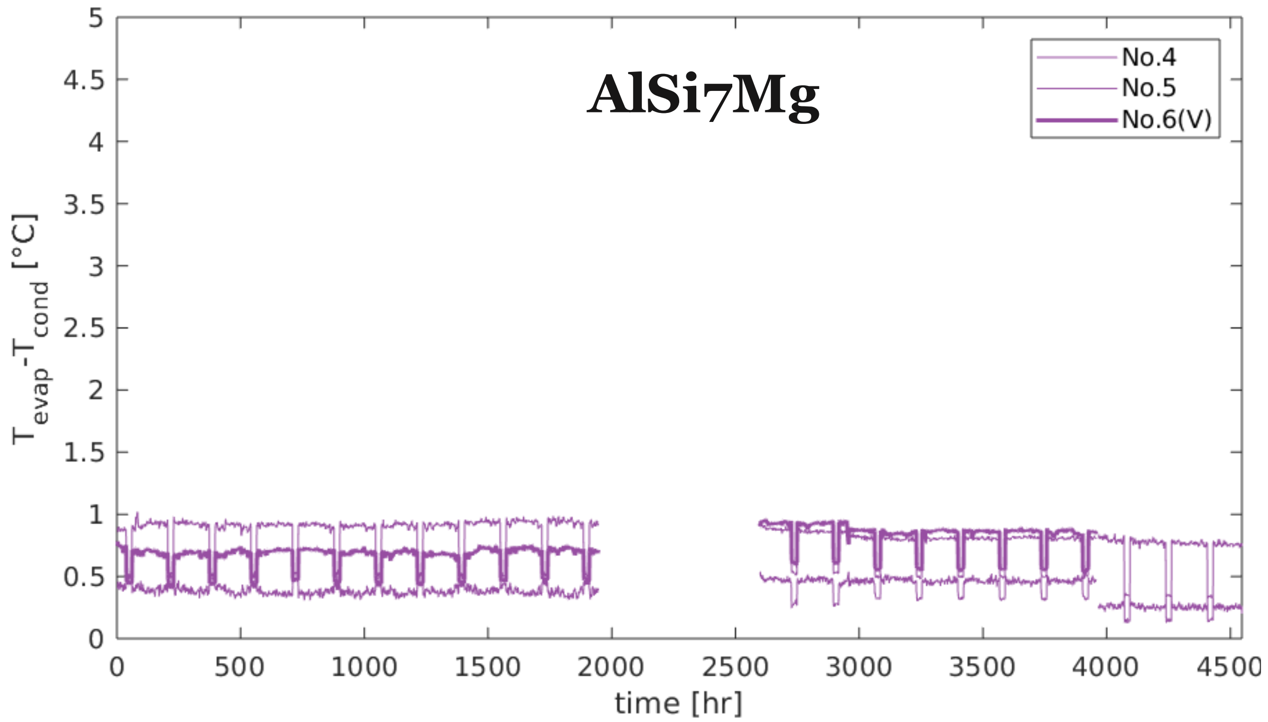
WP4 Characterisation

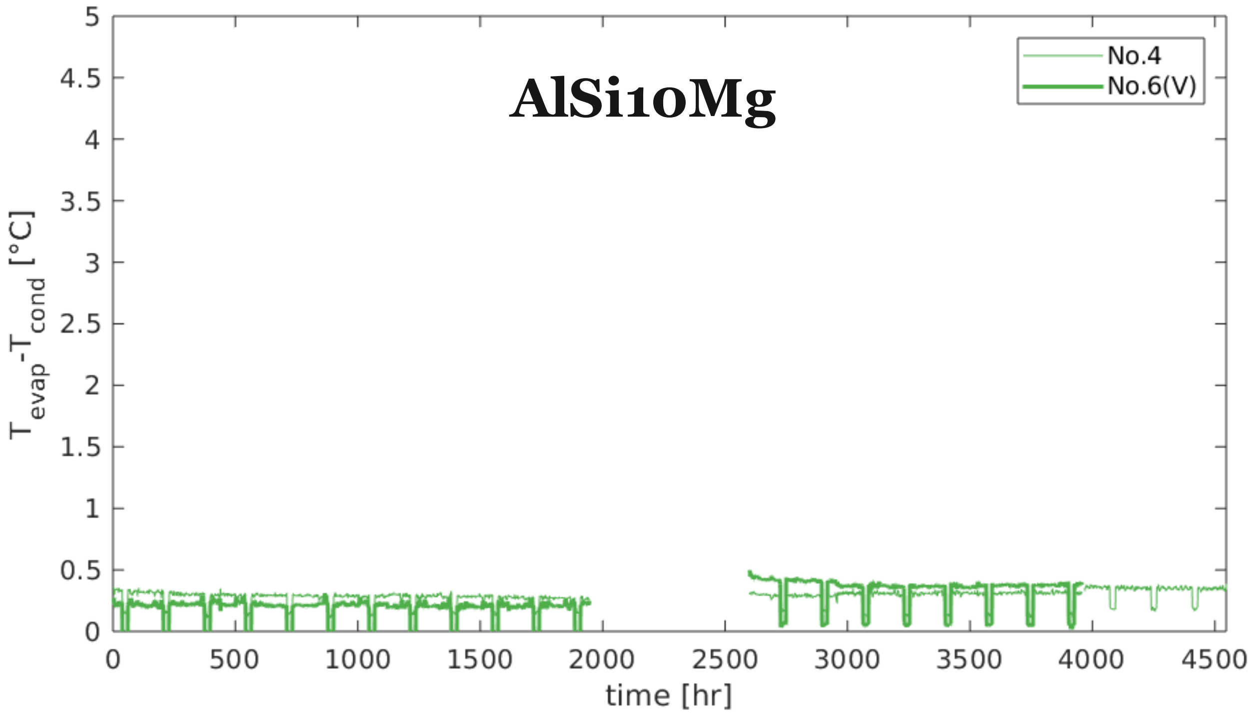
- **Gas Plug Test - Ammonia**

Valved samples removed after 4000 hrs for Corrosion Analysis







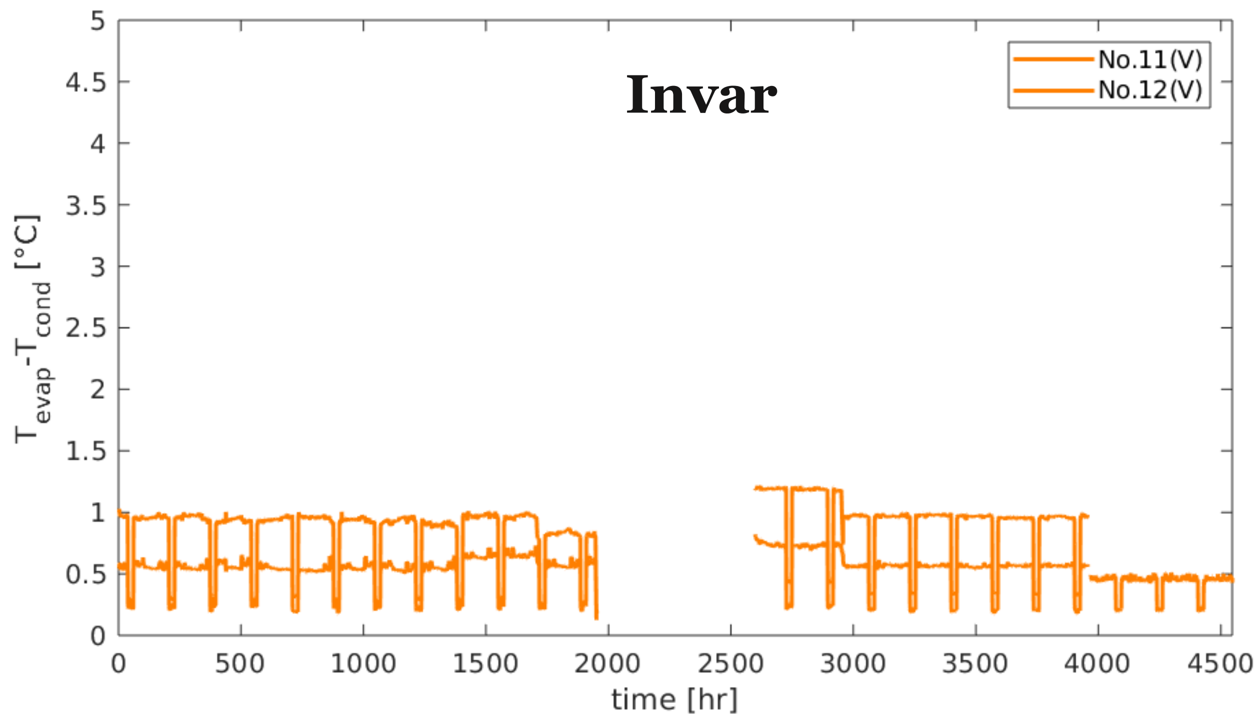


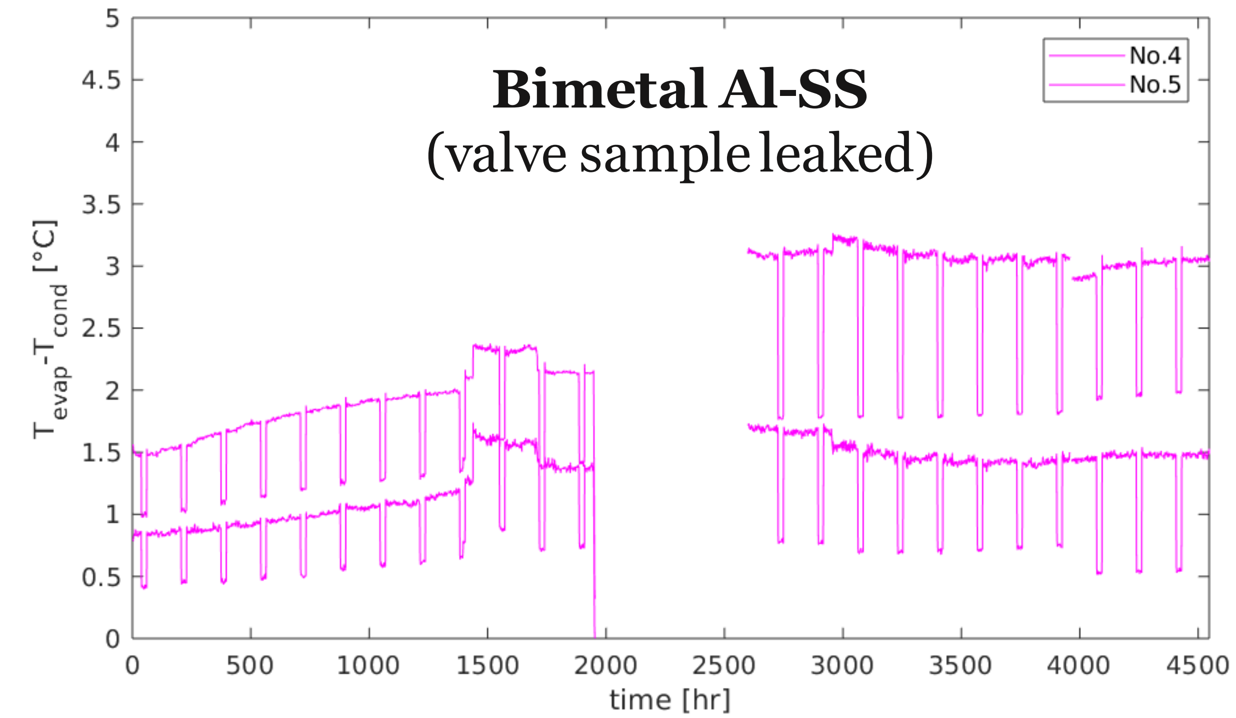
Bernal Institute

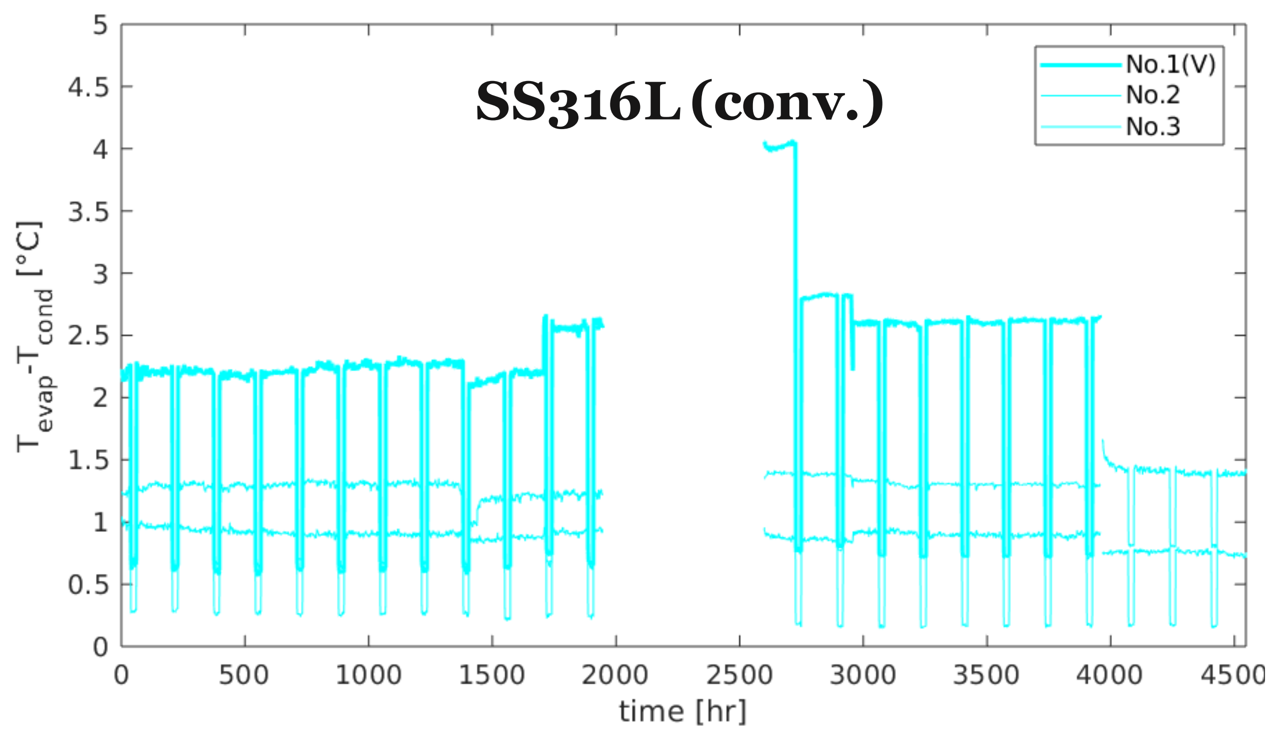
WP4 Characterisation

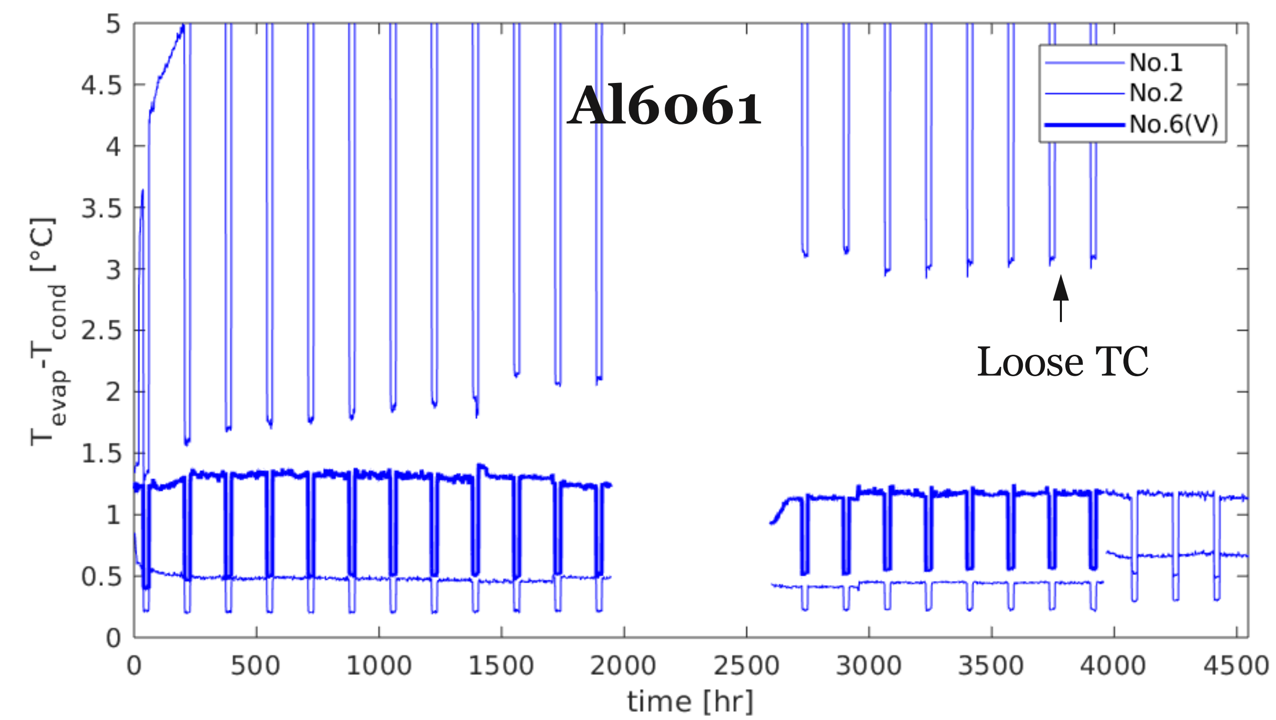
- **Gas Plug Test - Ammonia**

Valved samples removed after 4000 hrs for Corrosion Analysis



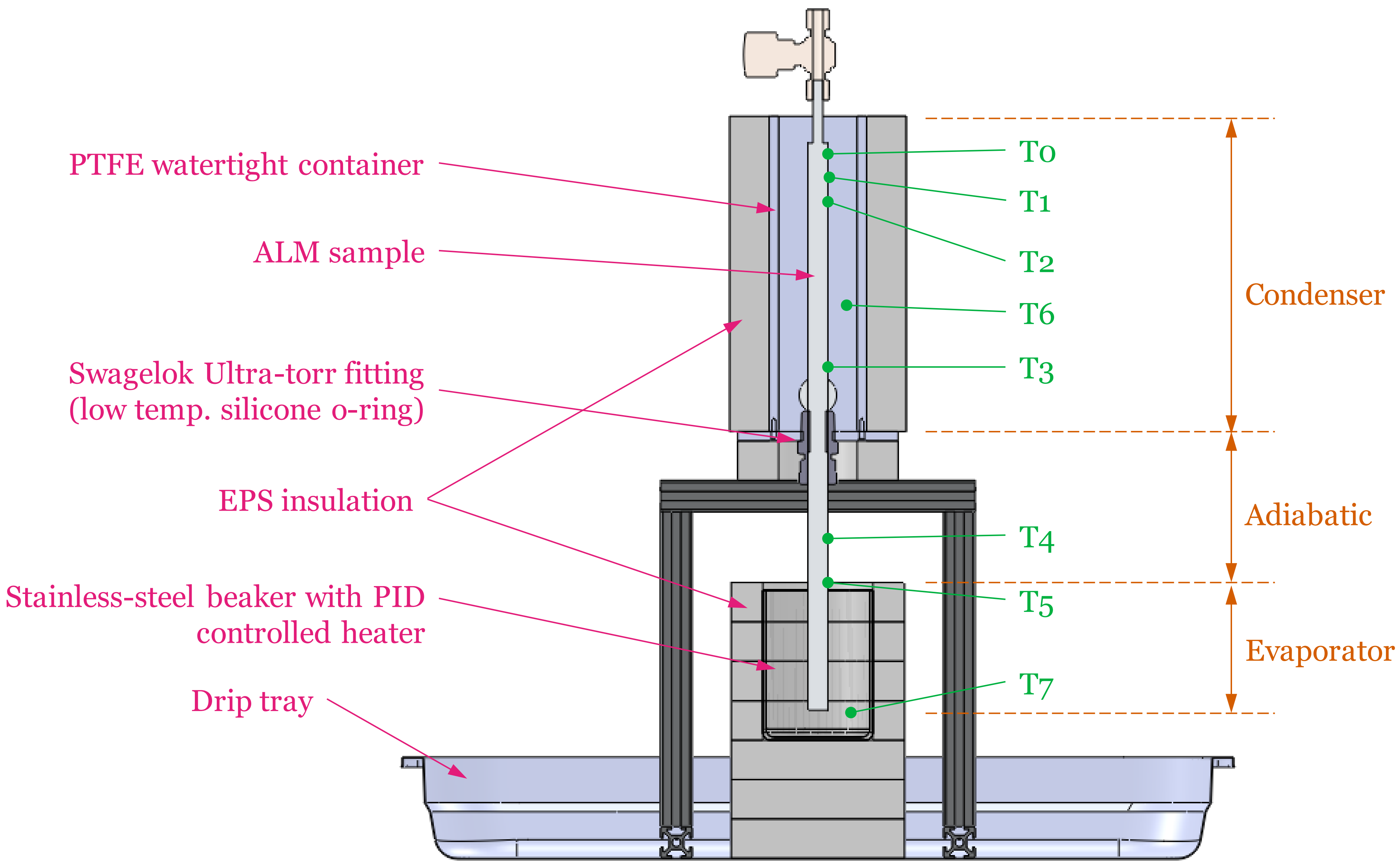






WP4 Characterisation

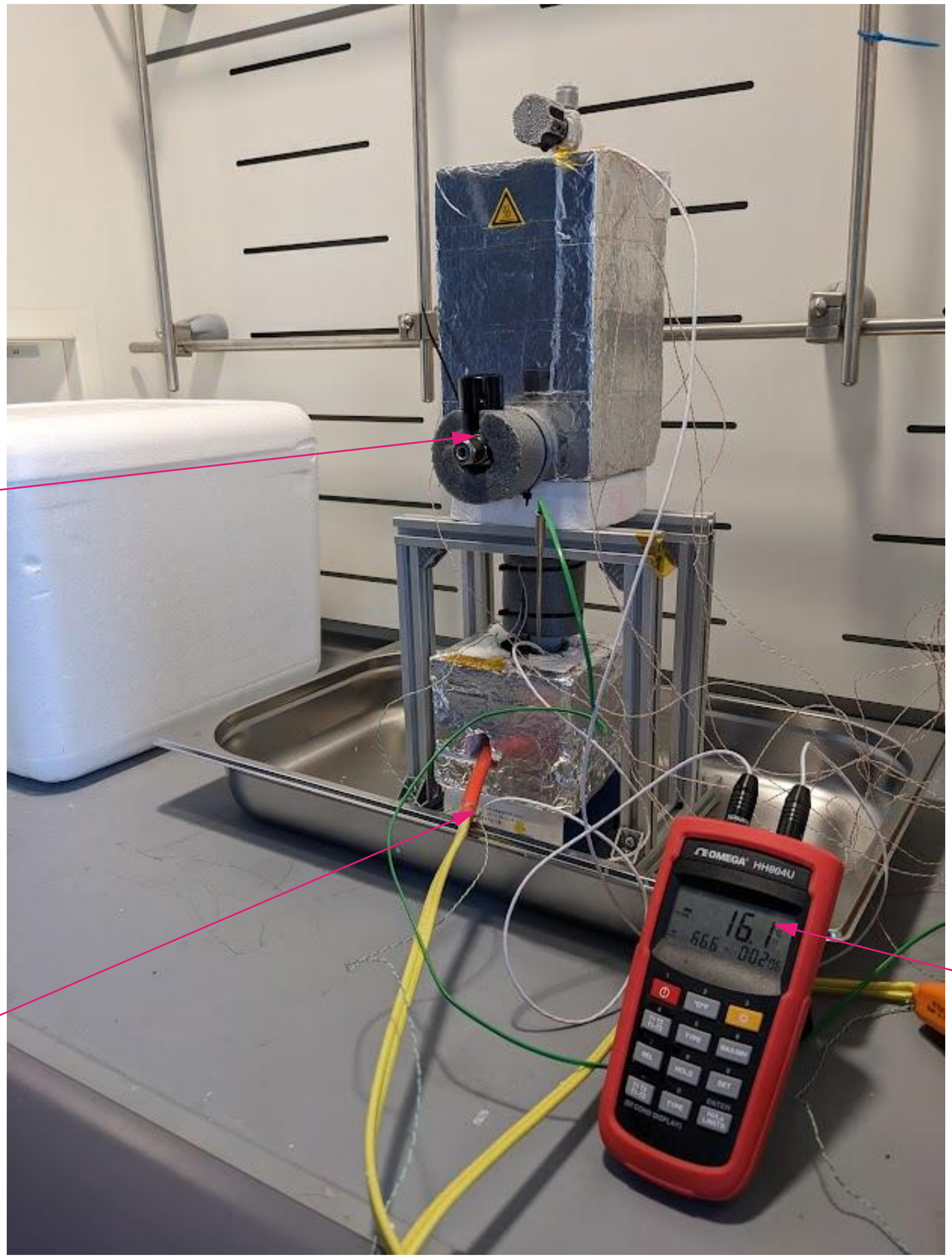
- **Gas Plug Test - Ammonia**
  - ALM AlSi7Mg-Ammonia sample at low temperature testing
  - Different cooling baths used to achieve low temperatures with Dry-Ice with IPA, Acetonitrile, or E.Glycol.



UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

WP4 Characterisation

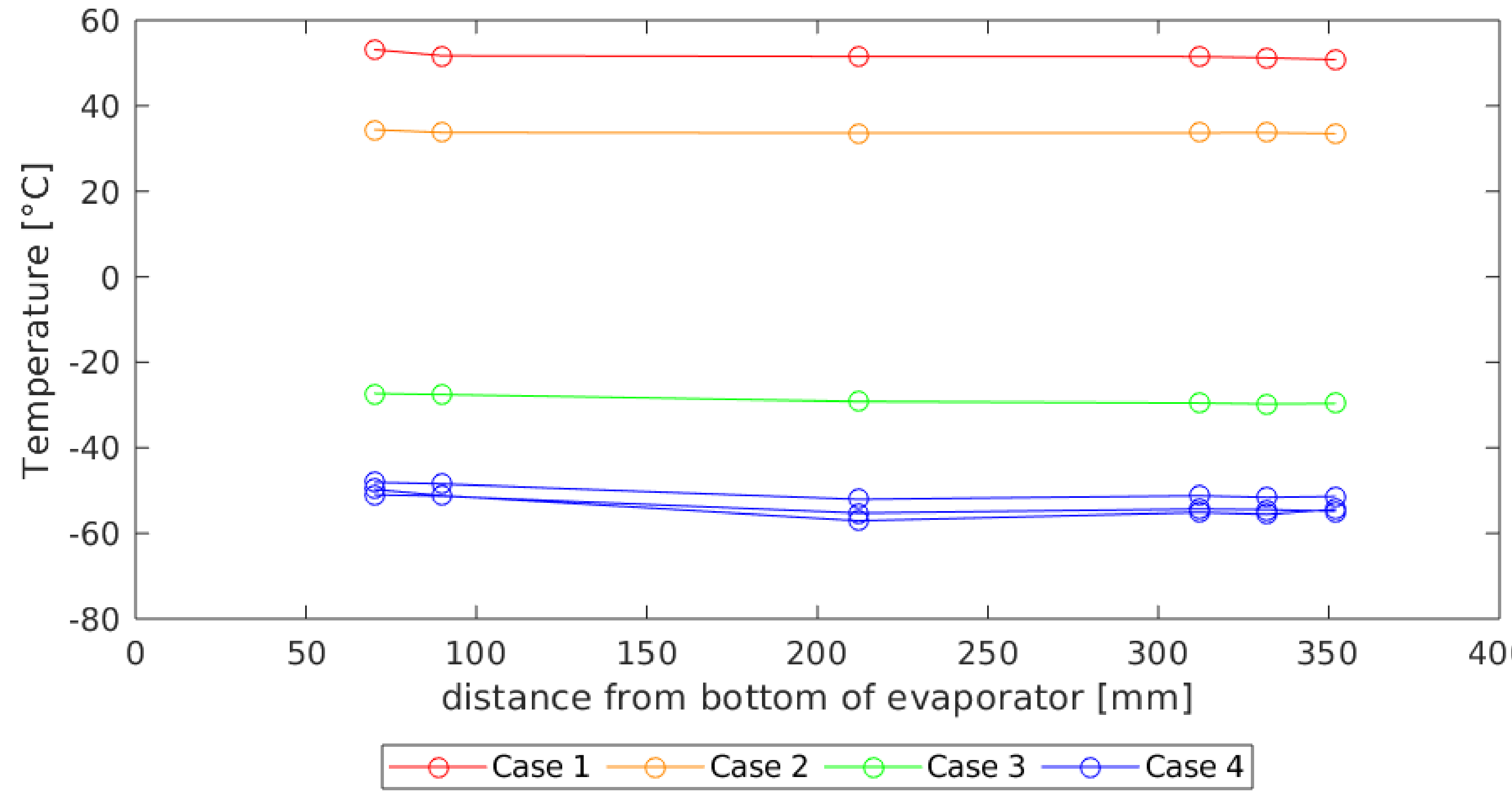
- **Gas Plug Test - Ammonia**
  - ALM AlSi7Mg-Ammonia sample at low temperature testing



WP4 Characterisation

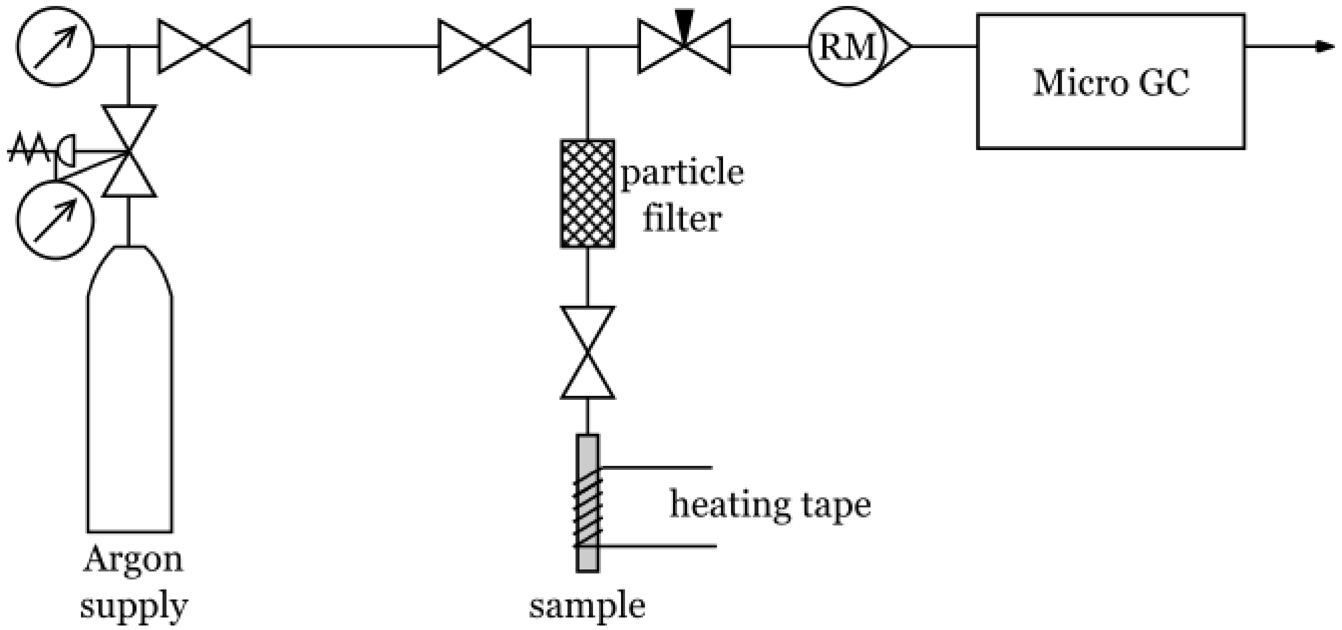
- **Gas Plug Test - Ammonia**
  - ALM AlSi7Mg-Ammonia sample at low temperature testing

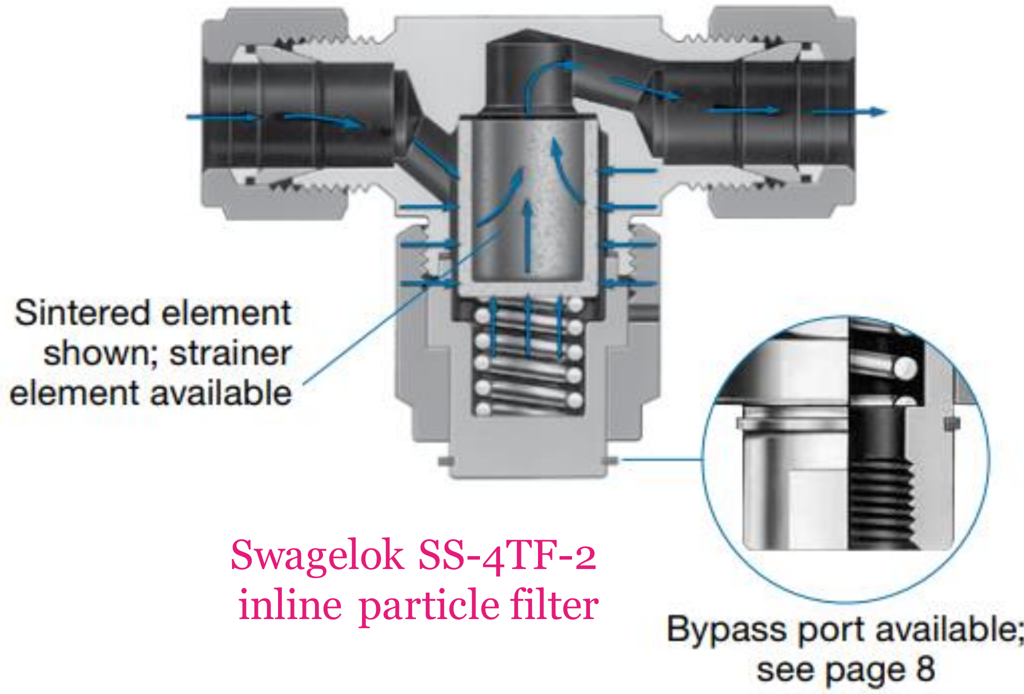
Test case	Evap. Temp. [°C]	Cond. Temp. [°C]	T5 – To [°C]
1	55	25	2.4
2	35	25	0.9
3	-20	-45	2.3
4	-45	-65	3.6



WP4 Characterisation

- **Gas Chromatography (GC) Analysis**
  - Performed in UL Chemical Sciences Department using Agilent Micro GC 3000A equipment.
  - Ability to detect and measure He, Ne, H_2, O_2, N_2, CH_4, Co, Co_2, C_2H_4, C_2H_6, C_2H_2, H_2S, C_3H_8, iC_4/nC_4, iC_5/nC_5, nC_6, nC_7.
  - Uses Argon as carrier and purge gas.
  - 2 µm particle filter placed after sample valve to catch any potential ALM particles.
  - Sample with H_2o cannot be tested.





Swagelok SS-4TF-2
inline particle filter

WP4 Characterisation

- **GC - Ammonia**
  - Results of gas sampling
  - PPM refers to concentration in **gas sample**, not full tube.

Metal		**Gases detected [ppm]**		
		CO	$\mathbf{H_2}$	$\mathbf{N_2}$
Conventional	SS316L	901	1064	5351
	Al6061-T6			5805
ALM	AlSi7Mg			481
	AlSi10Mg		18	1216
	Invar			132
	SS316L			627
	Ti6Al4V	183	188	
Bimetallic	Al/SS	*not tested*		

- Gas slug was only detected in 1-2 sample volumes and only ammonia signal was seen afterwards.

WP4 Characterisation

- **GC - Ammonia**
  - Estimation of overall working fluid purity from filling volume:

Metal		**Working fluid impurity, *f* [ppm]**
Conventional	SS316L	333.1
	Al6061-T6	36.6
ALM	AlSi7Mg	3.2
	AlSi10Mg	5.9
	Invar	2.4
	SS316L	9.9
	Ti6Al4V	3.4
Bimetallic	Al/SS	*not tested*

WP4 Characterisation

- **GC - Ammonia**
  - Mainly N_2 detected in the top of all Ammonia cases.
  - Potential sources include:
    - Gas cylinder: 99.98% purity, further purified by inline purifier designed for NH_3 and C_3H_6, which removes H_2O, O_2, CO_2 and organics >C_4, but not N_2.
    - Purifier is factory-filled with N_2 as an inert gas for shipping which is purged from the device during a conditioning period before operation. From manual, "*if contaminant level is high for N_2, but low for H_2O and O_2, the purifier may not have been completely purged of the factory-filled gas*" – considered very likely in this case.
    - N_2 was used as filling rig purging gas which may have been getting trapped somewhere during vacuum evacuation and then outgassing during fill.

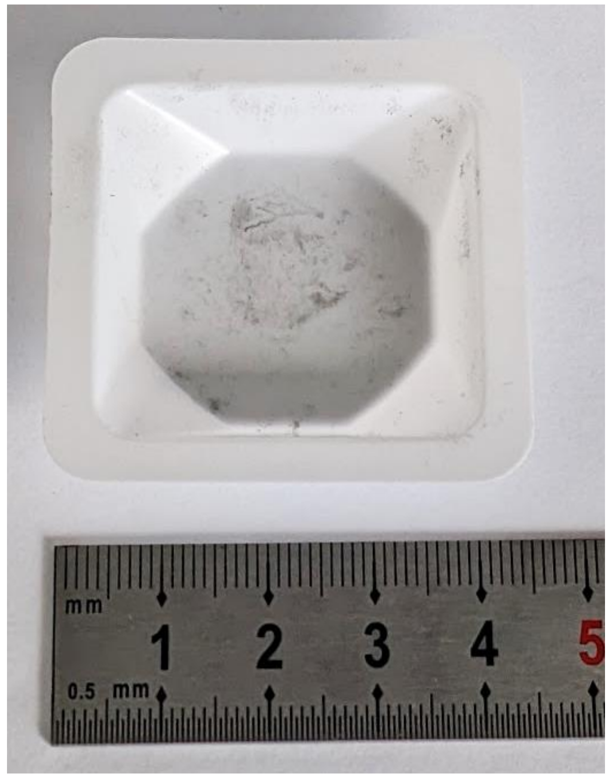
  - Ammonia samples had additional purge fill cleaning step.
  - Overall NCG concentration was quite low, and it did not have a significant impact on the testing.

WP4 Characterisation

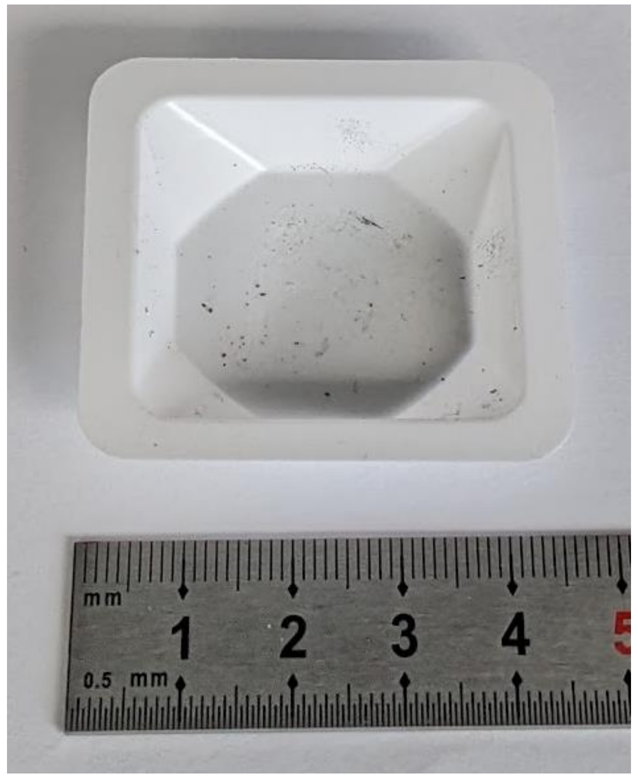
- **GC - Ammonia**
  - Loose particles in samples.
  - Mass of filter weighed before and after gas sampling and purging.
  - Pipe sectioned at condenser with pipe cutter and any loose particles were collected on weighing boat.

Metal	**Gas purging**			**Pipe sectioning**			**Total mass [mg]**
	Filter mass before [mg]	**Filter mass after [mg]**	**Diff. [mg]**	**Boat mass before [mg]**	**Boat mass after [mg]**	**Diff. [mg]**	
AlSi7Mg	6423.4	6423.3	-0.1	672.2	673.1	0.9	0.8
AlSi10Mg	6412.4	6412.7	0.3	663.2	664.1	0.9	1.2
Invar	6416.4	6416.8	0.4	651.7	652.0	0.3	0.7
SS316L	6429.0	6429.3	0.3	614.1	619.7	5.6	5.9
Ti6Al4V	6439.7	6440.4	0.7	642.3	644.1	1.8	2.5

  - In general, very small mass found for ammonia samples.



SS316LALM - Ammonia



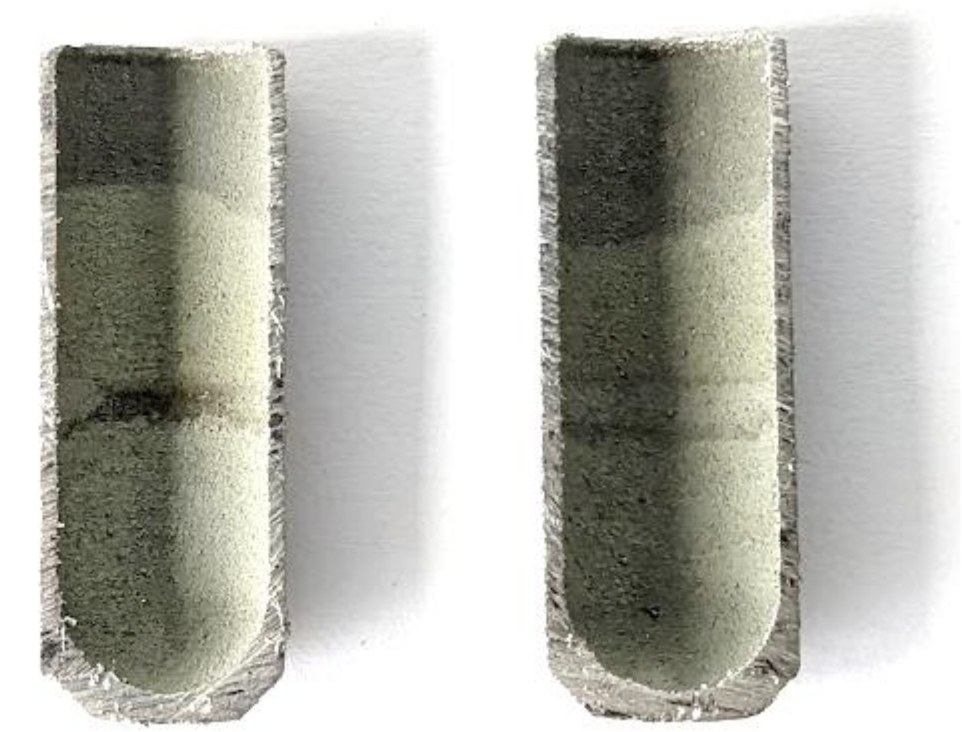
Ti6Al4V - Ammonia

WP4 Characterisation

- **Sectioning - Ammonia**
  - Samples cut at evaporator with pipe cutter and carefully sectioned.
  - Ammonia samples currently undergoing XPS.

SS316L ALM
Light stain at L.-V. interface

Ti6Al4V
Nothing of note



Invar
Light green colour in L. zone

WP4 Characterisation

- **Sectioning - Ammonia**
  - Samples cut at evaporator with pipe cutter and carefully sectioned.
  - Ammonia samples currently undergoing XPS.

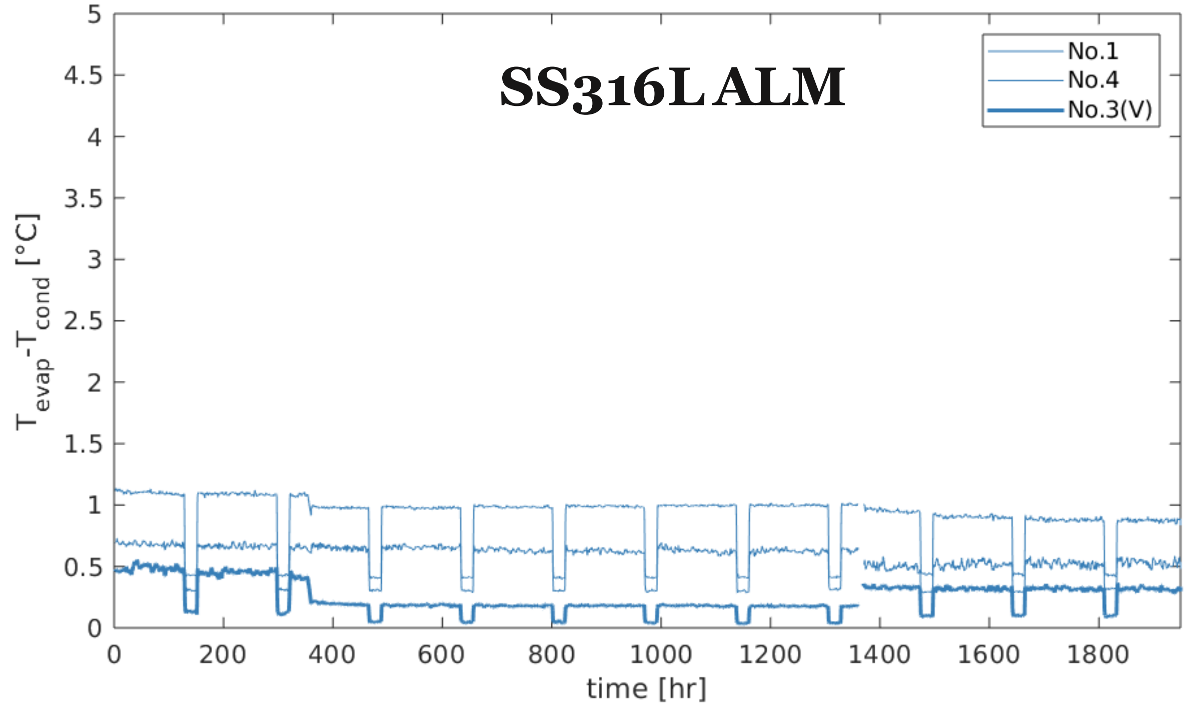
AlSi7Mg
Slight blue tint in L. zone

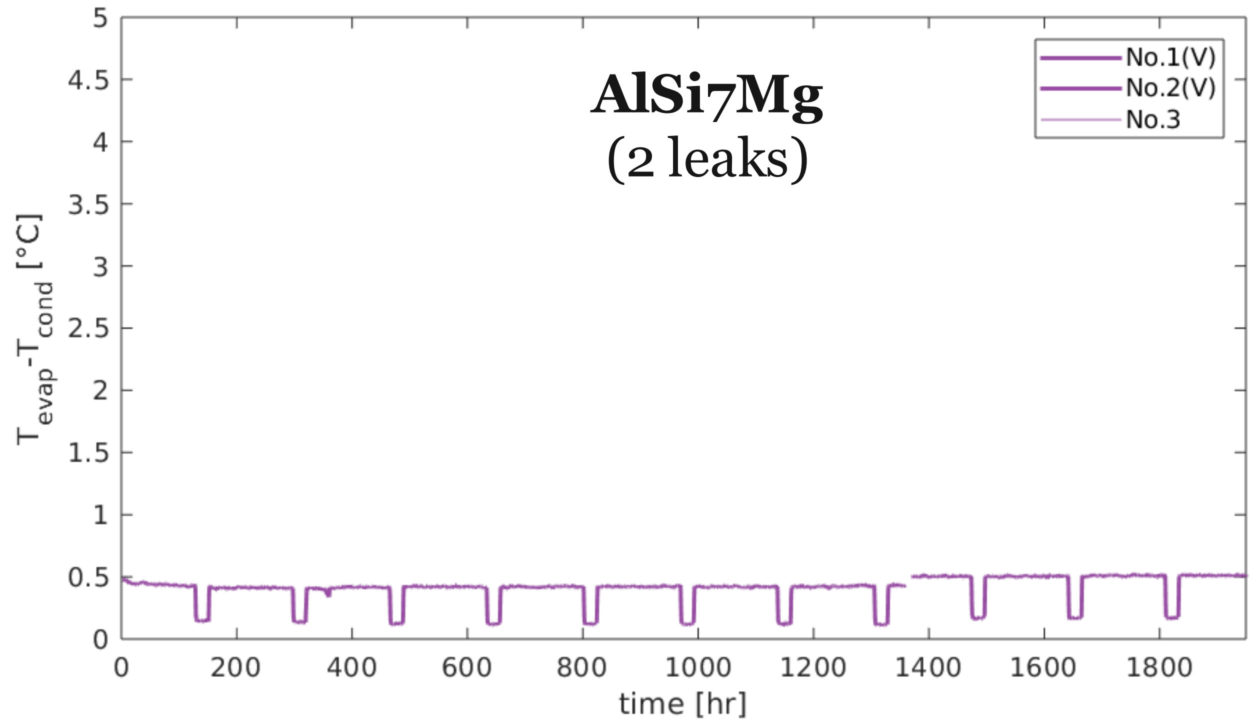
AlSi10Mg
Slight brown tint in L. zone

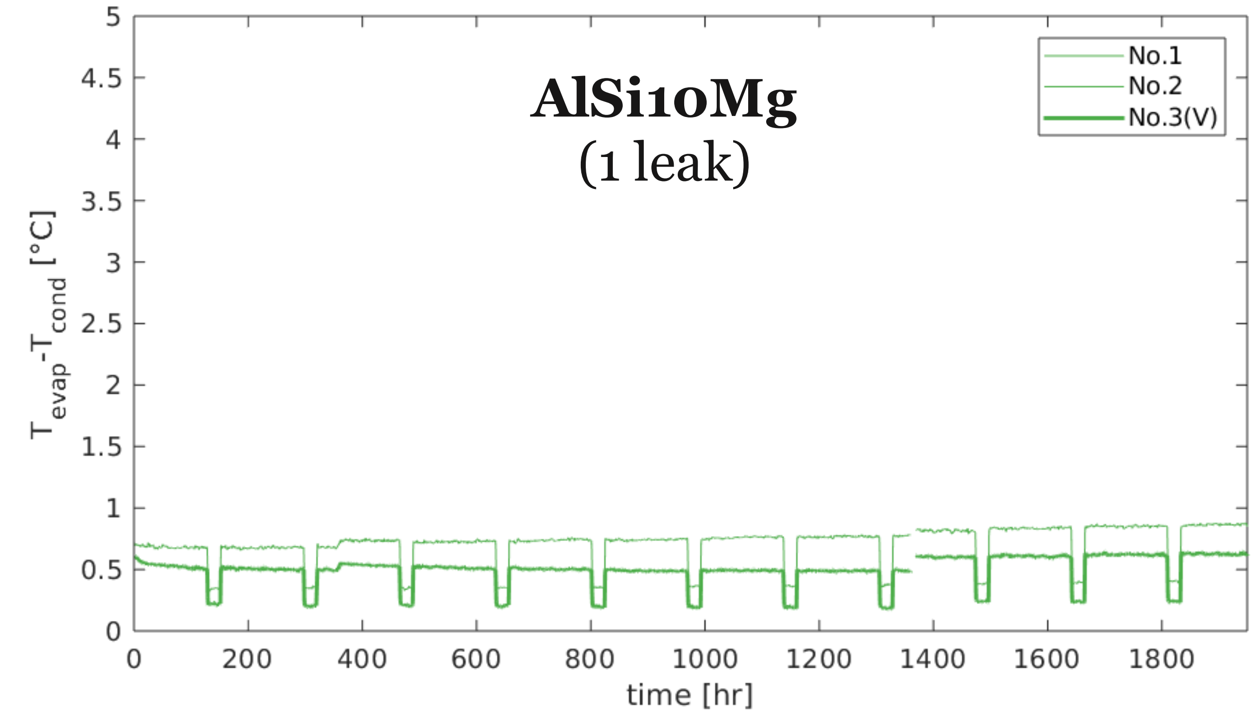
Bimetal Al-SS
Weld colouration (leak sample)

WP4 Characterisation

- **Gas Plug Test - Ammonia**



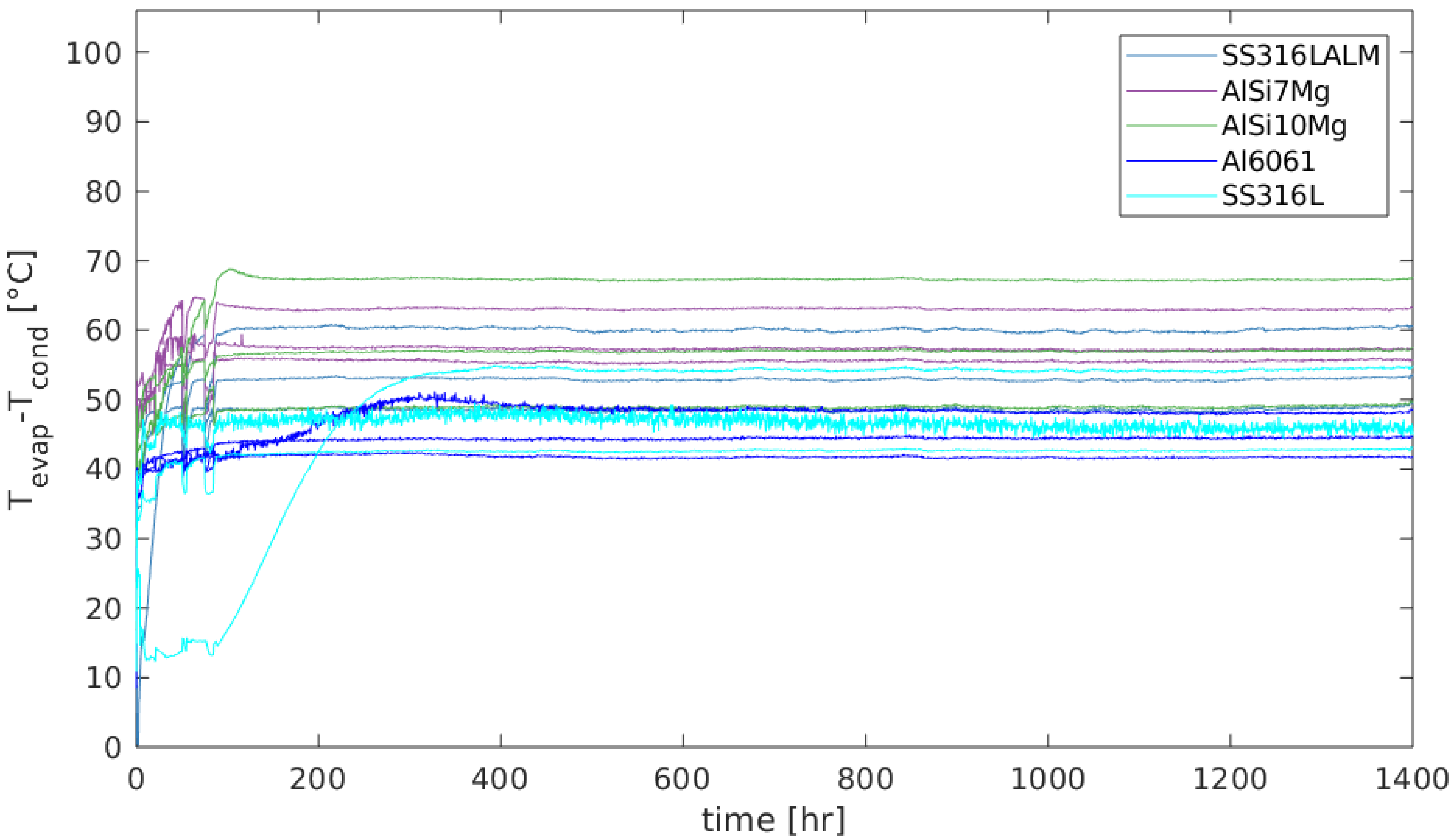




Bernal Institute

WP4 Characterisation

- **Gas Plug Test - Ethylene glycol**
  - All samples showed very large ΔT quickly after startup

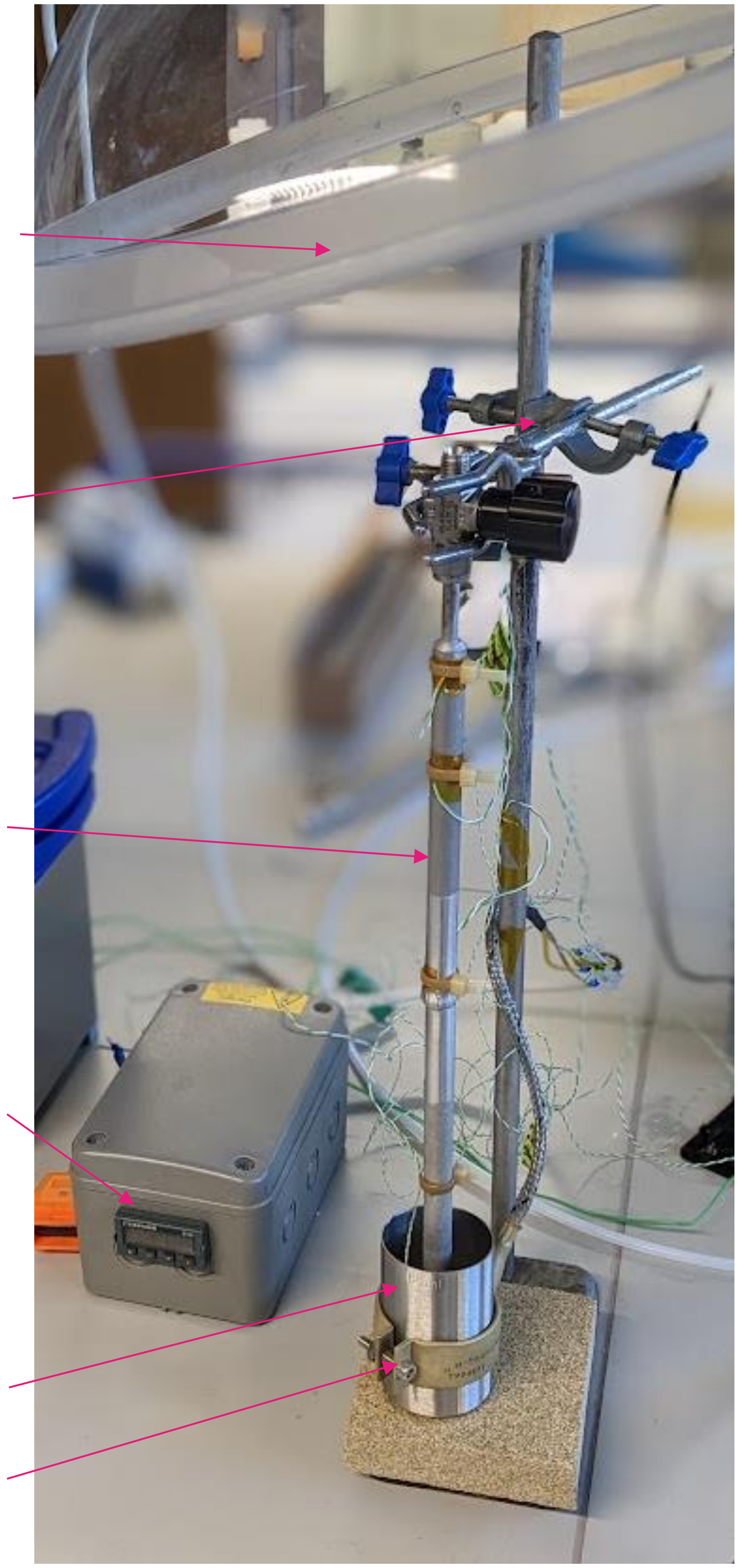


UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH
Bernal Institute

WP4 Characterisation

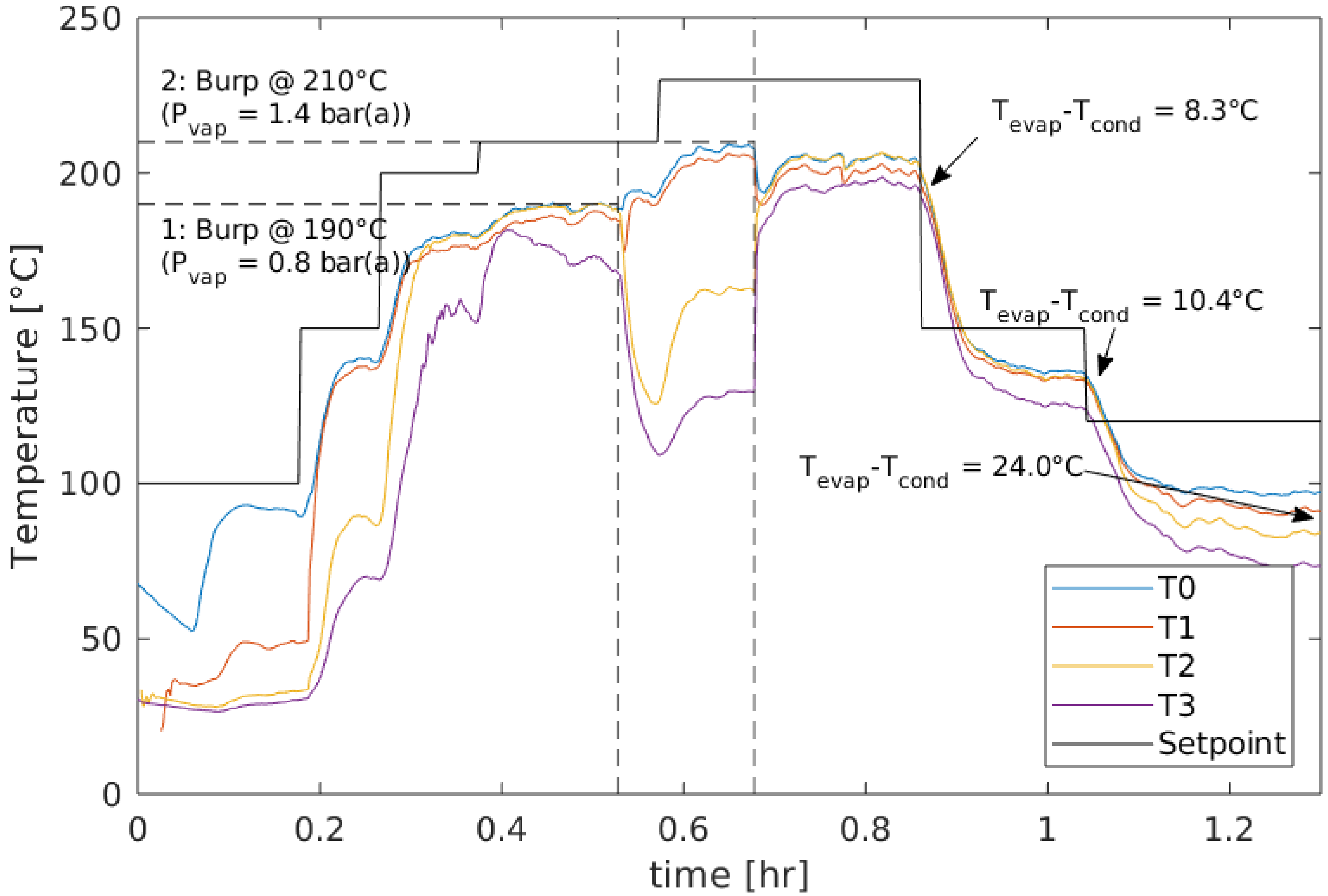
- **Gas Plug Test - Ethylene glycol**
  - 2 rounds of FPT using the Filling Rig for Al6061 sample no. 4.
  - Dry-ice/IPA bath used to freeze ethylene glycol inside the sample between vacuum cycles.
  - No change in filling mass after FPT.

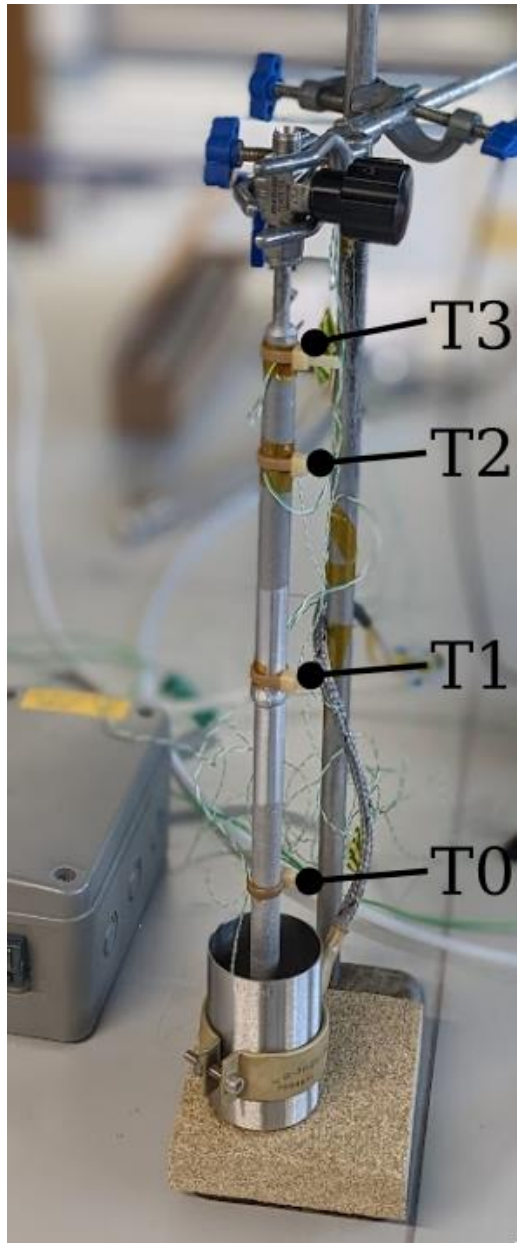
Test	$T_{evap.} - T_{cond.}$ [°C]
Before FPT @ 120°C	22.1
After FPT @ 120°C	21.2



WP4 Characterisation

- **Gas Plug Test - Ethylene glycol**
  - ‘Burping’ of Al6061 sample no. 4.

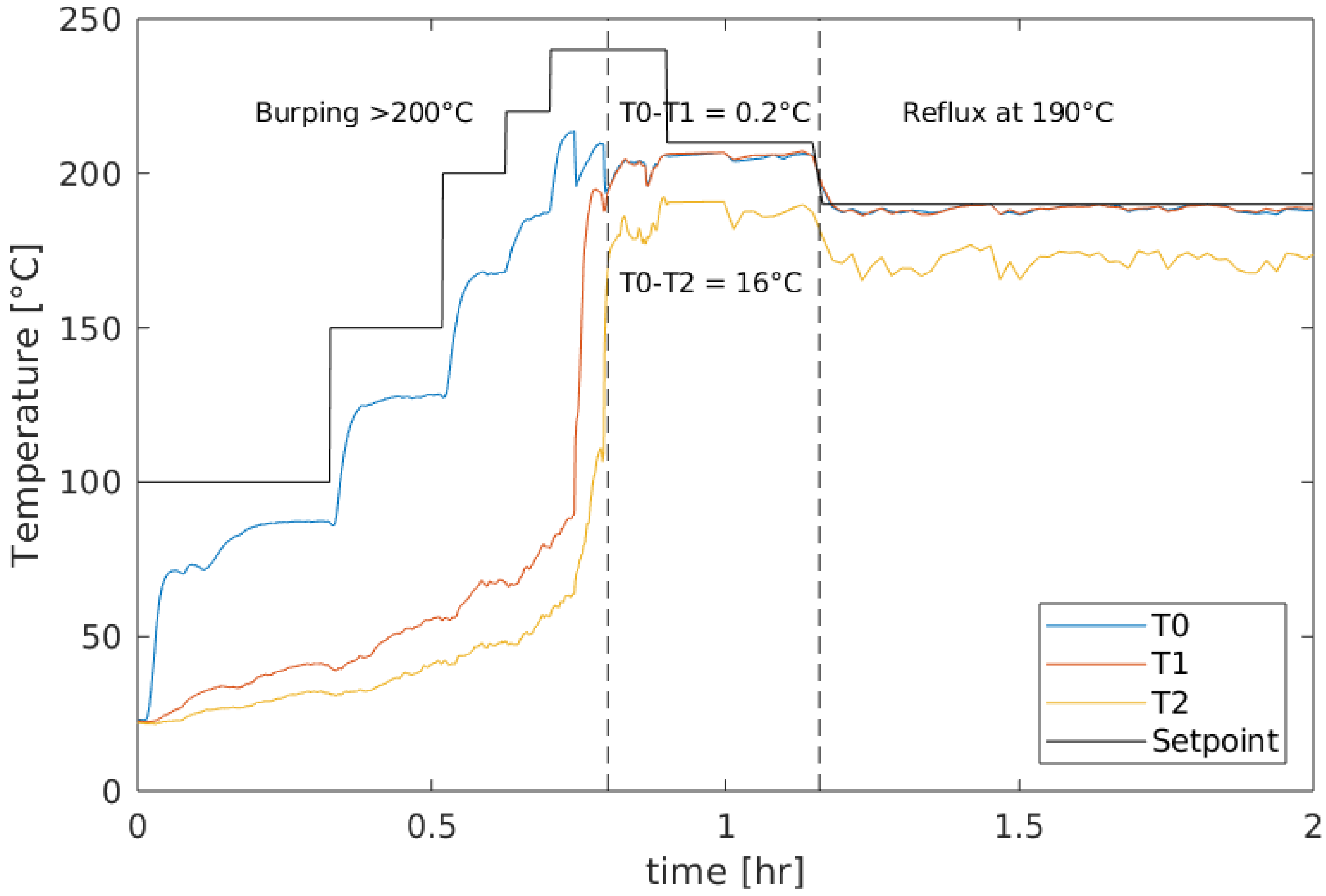


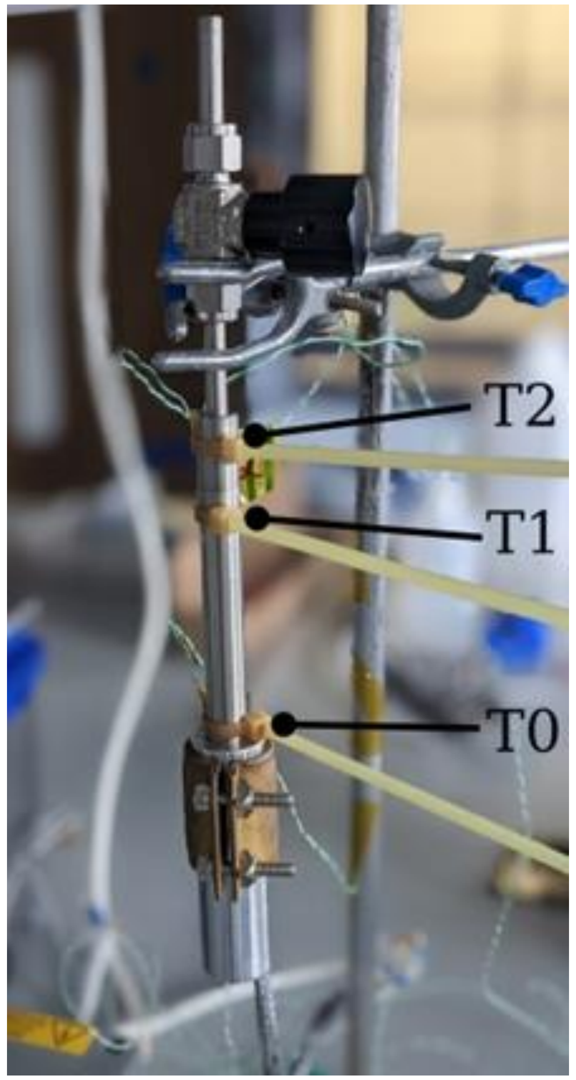


  - No performance improvement with replaced in Gas Plug Rig.

WP4 Characterisation

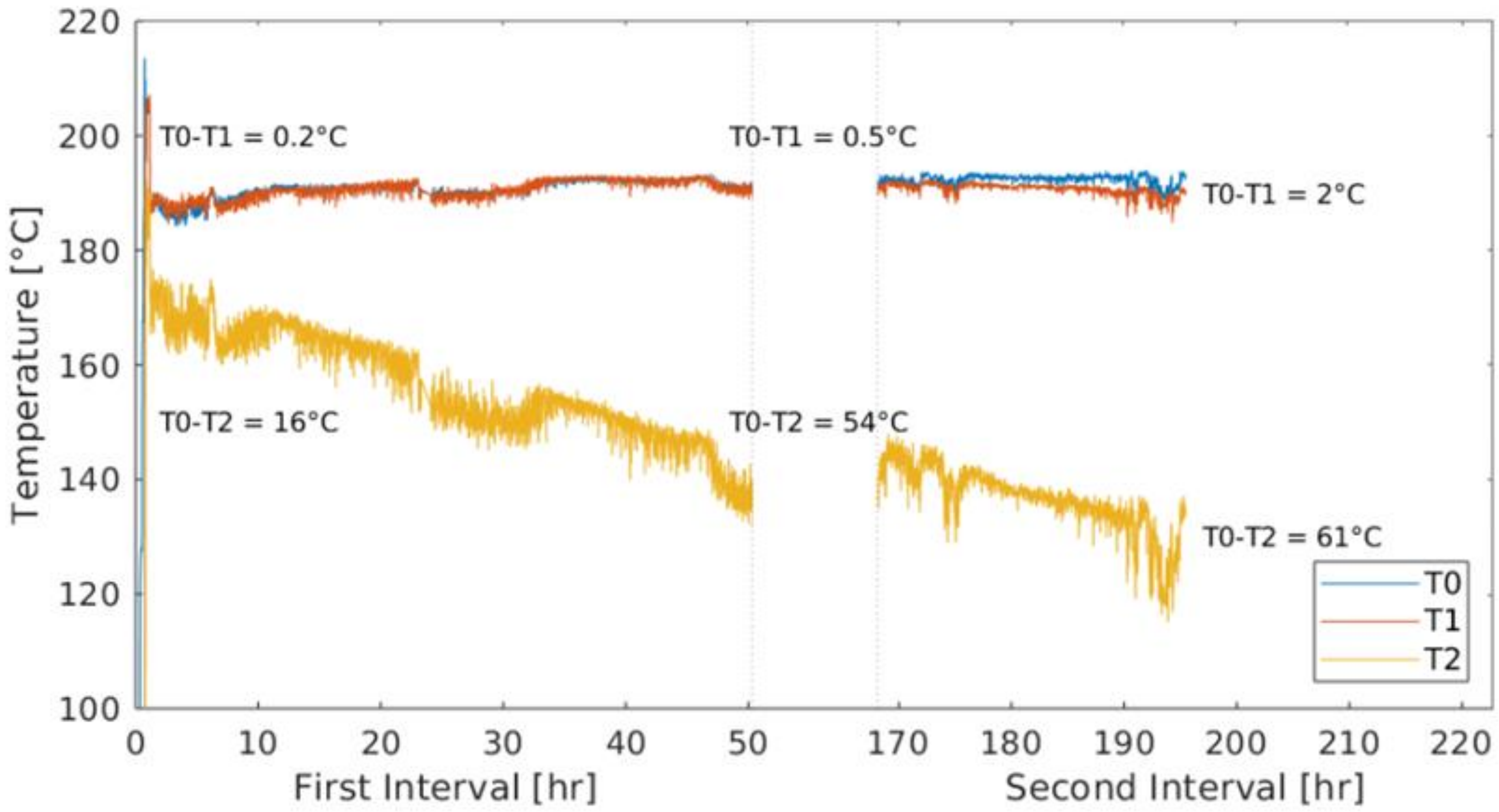
- **Gas Plug Test - Ethylene glycol**
  - ‘Burping’ of <u>unused</u> SS316L sample

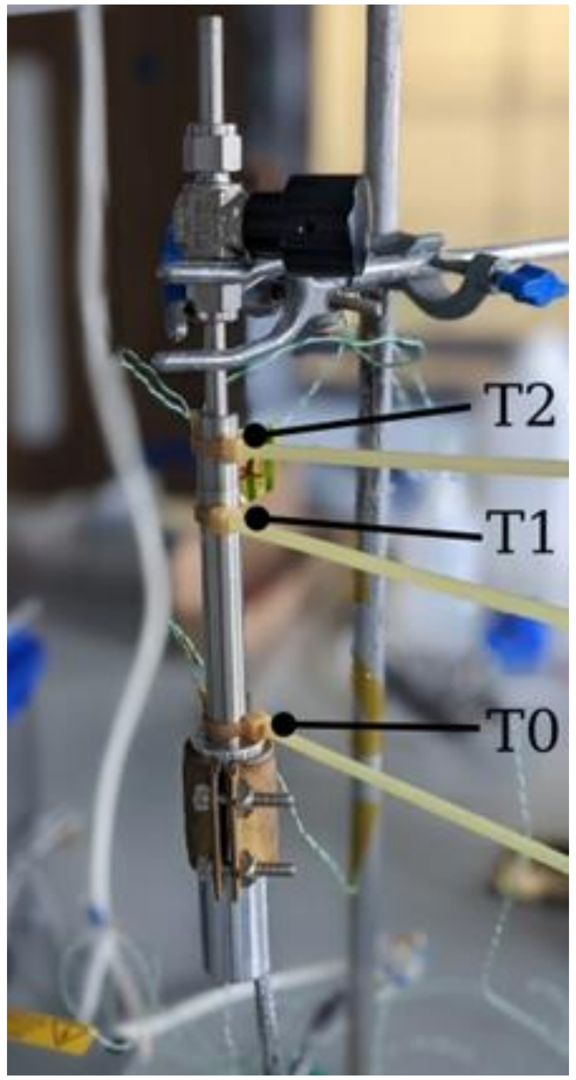




WP4 Characterisation

- **Gas Plug Test - Ethylene glycol**
  - ‘Burping’ of unused SS316L sample





WP4 Characterisation

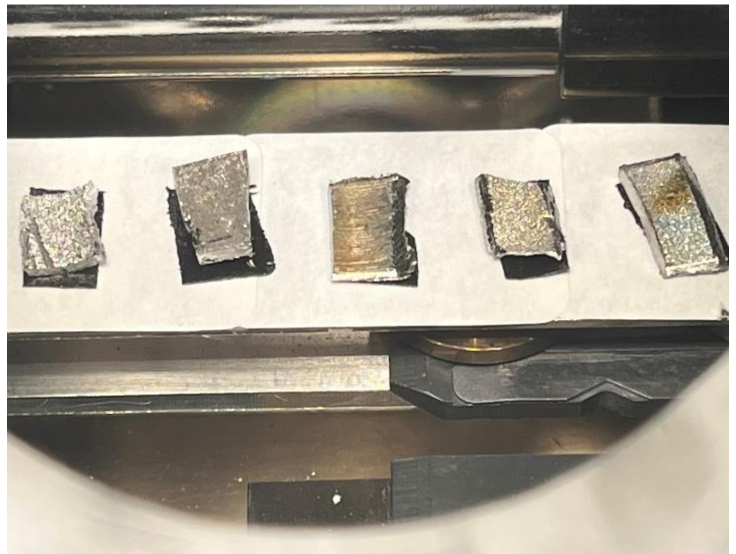
- **Sectioning - Ethylene glycol**
  - Previous SS316L sample cut at evaporator with pipe cutter and carefully sectioned.

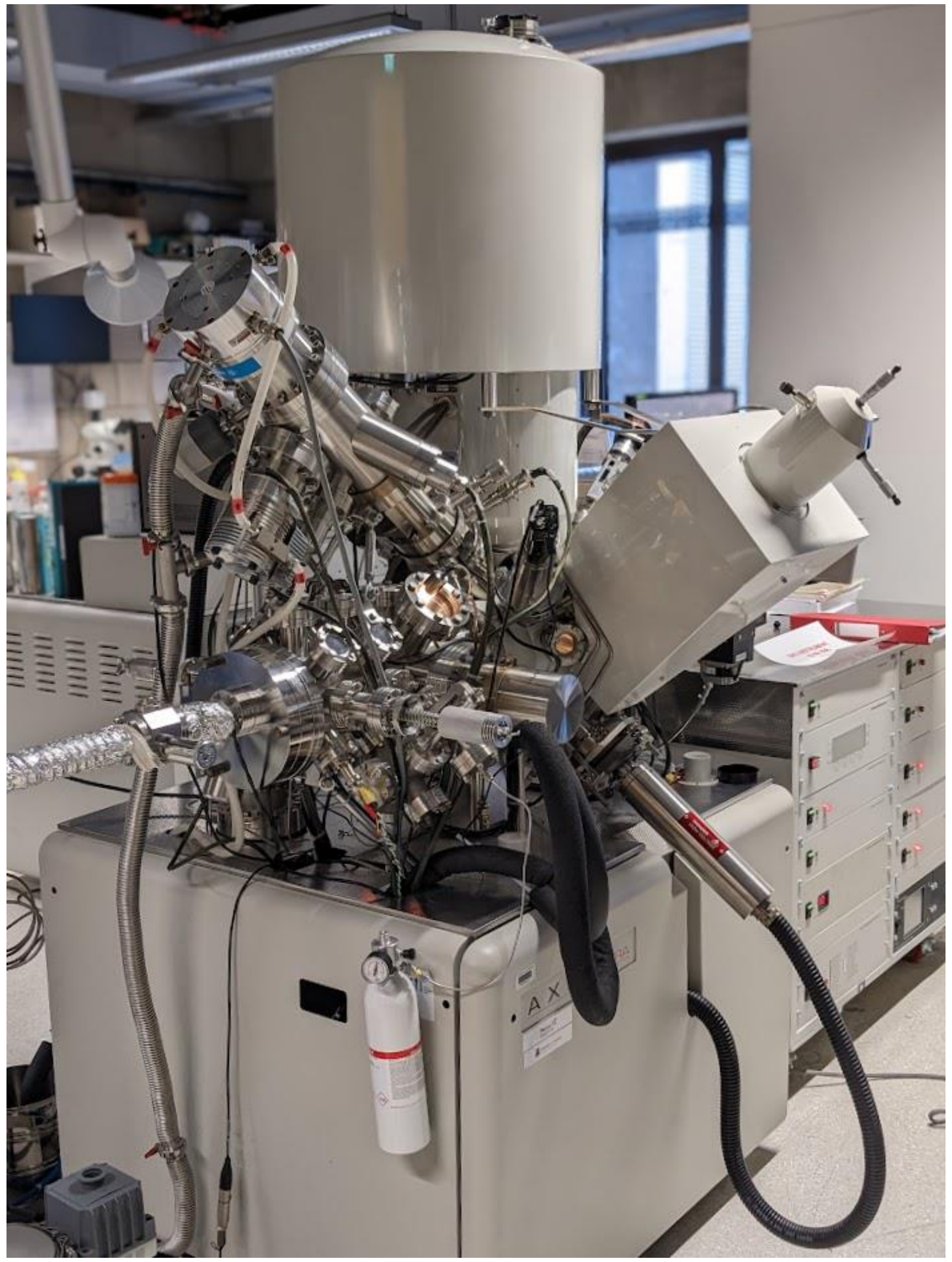
SS316L conv.
Brown corrosion in L.-V. interface region

New E.Glycol VS. SS316L E.Glycol

WP4 Characterisation

- **XPS**
  - Performed in UL using Kratos Axis Ultra XPS.
  - Analysis area is approximately 1 mm^2 and depth of analysis is ~ 10 nm.
  - Areas of interest carefully cut from samples.
  - Samples with interesting results from Gas Plug but no GC were given priority.
  - Invar samples cannot be analysed with XPS due to magnetic properties of material, but EDX will be performed.





UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

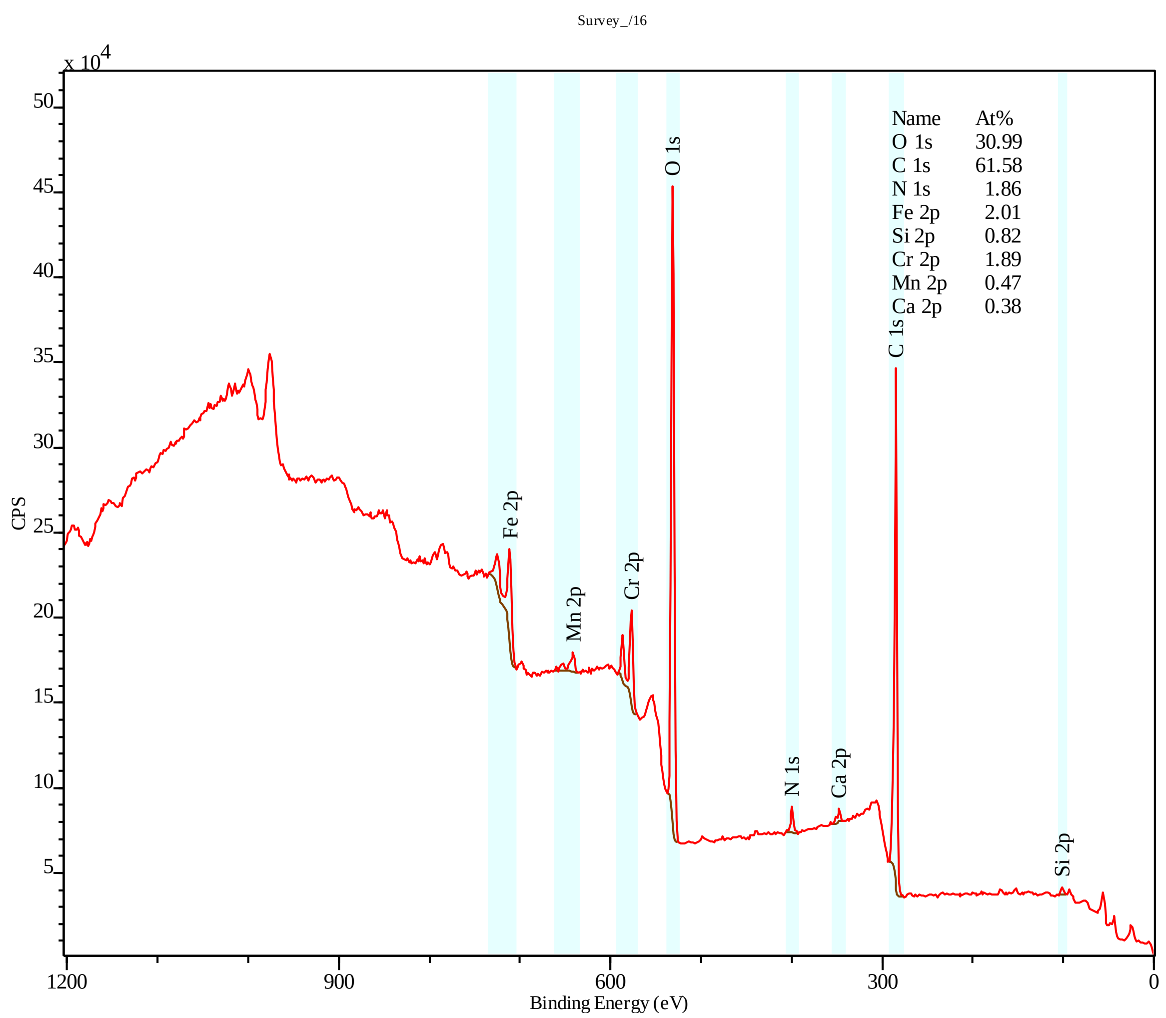
WP4 Characterisation

- **XPS - Ethylene glycol**
  - Section in corroded area from previous SS316L sample cut.
  - High concentrations of oxides (Fe_2O_3, Cr_2O_3, $Cr(OH)_3$).
  - C levels consistent with Adventitious Carbon on Metal.

  - Information available in literature states that ethylene glycol has a natural tendency to degrade at high temperatures.
  - Above 135°C, thermal degradation/decomposition can occur due to the production of organic acids such as acetic, formic, oxalic, and glycolic acid.

$$\underset{\text{MEG}}{C_2H_6O_2} \xrightarrow{Heat+O_2} \underset{\text{Oxalic acid}}{C_2H_2O_4} + \underset{\text{Glycolic acid}}{C_2H_4O_3} + \underset{\text{Formic acid}}{CH_2O_2}$$

  - This results in the lowering of the pH of the fluid and corrosion of metallic components.



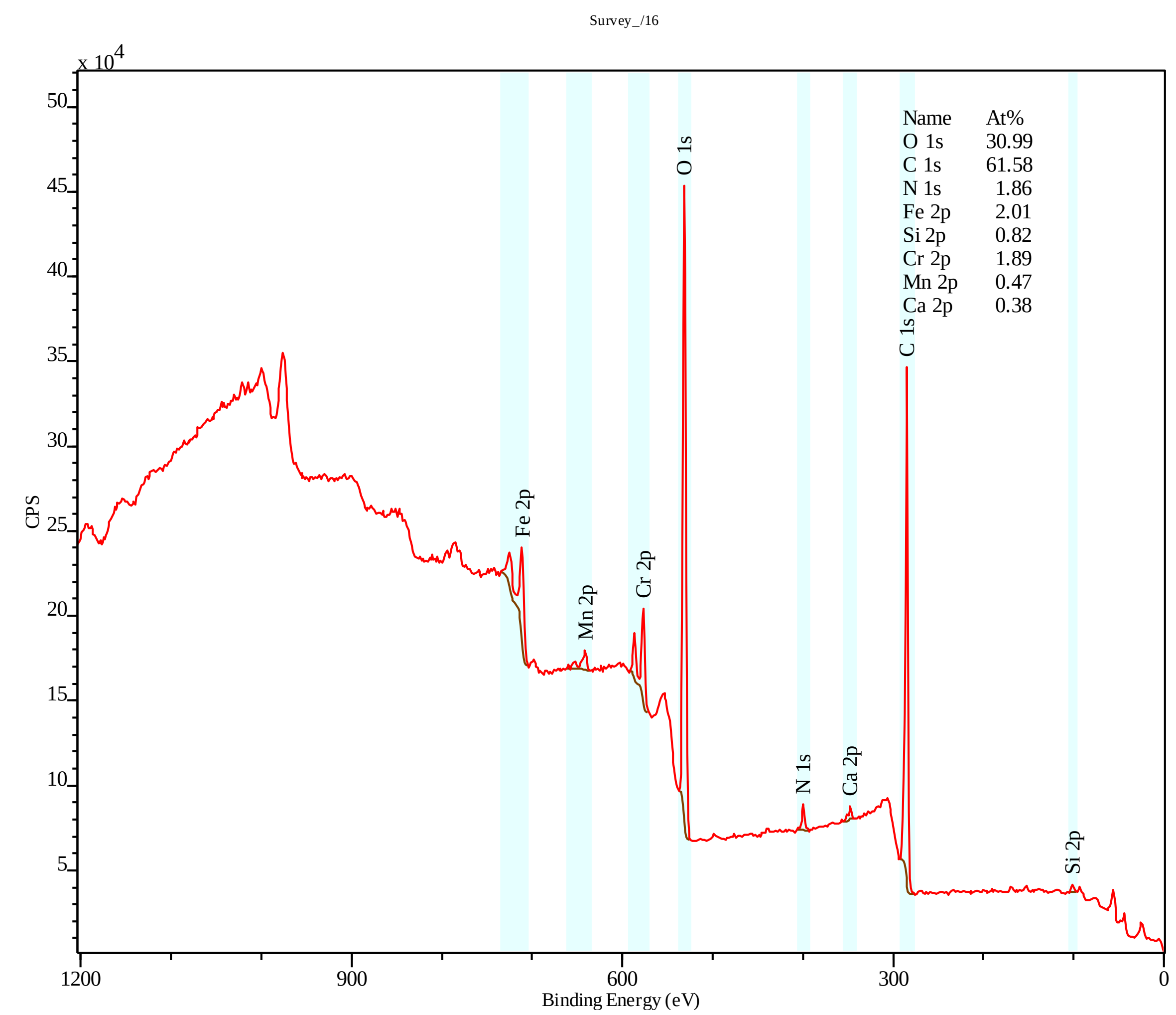
WP4 Characterisation

- **XPS - Ethylene glycol**
  - At temperatures > 157°C, thermal degradation without oxidation is possible.

$$\underset{\text{MEG}}{C_2H_6O_2} \xrightarrow{Heat} \underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Water}}{H_2O}$$

$$\underset{\text{MEG}}{C_2H_6O_2} \xrightarrow{Heat} \underset{\text{Ethylene oxide}}{C_2H_4O} + \underset{\text{Water}}{H_2O}$$

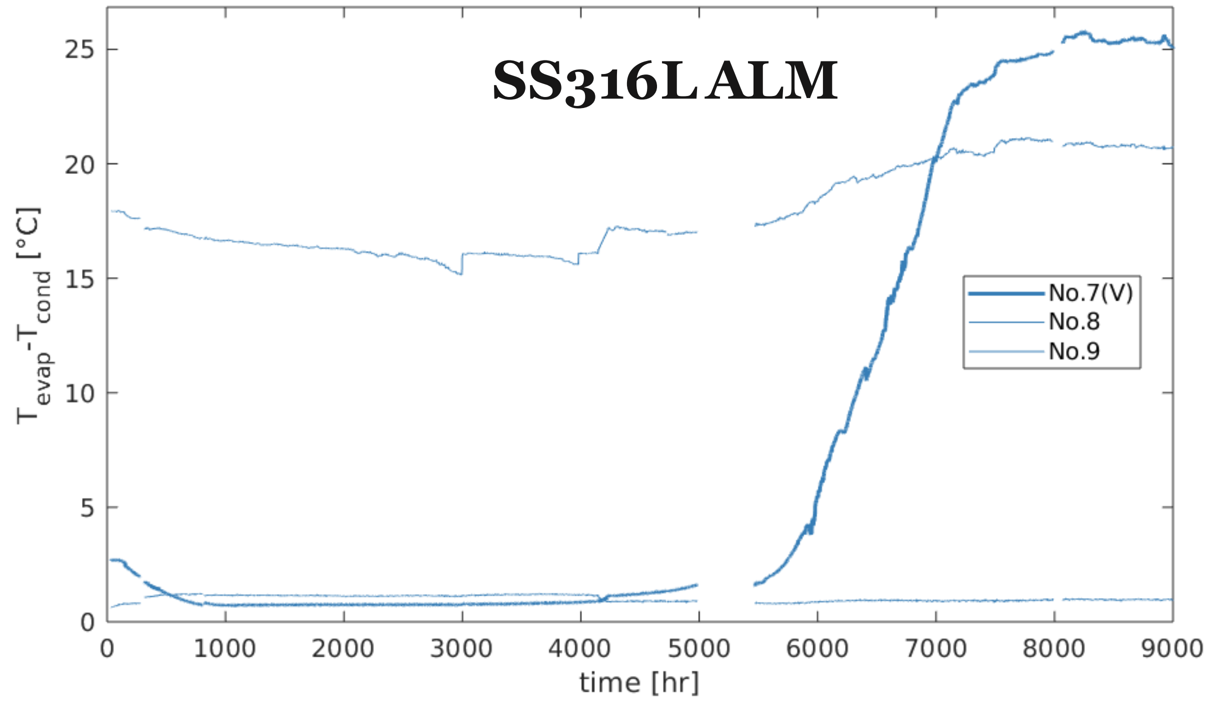
  - As heat flux and temperature increases, this decomposition becomes more intense.
  - Based on observed results, Ethylene Glycol is not a suitable working fluid for long-term operation at high temperatures for two-phase devices.
  - Although it may be more stable at lower temperatures, the existence of other fluids with good chemical compatibility and relatively higher merit numbers limits its usefulness in this range also.

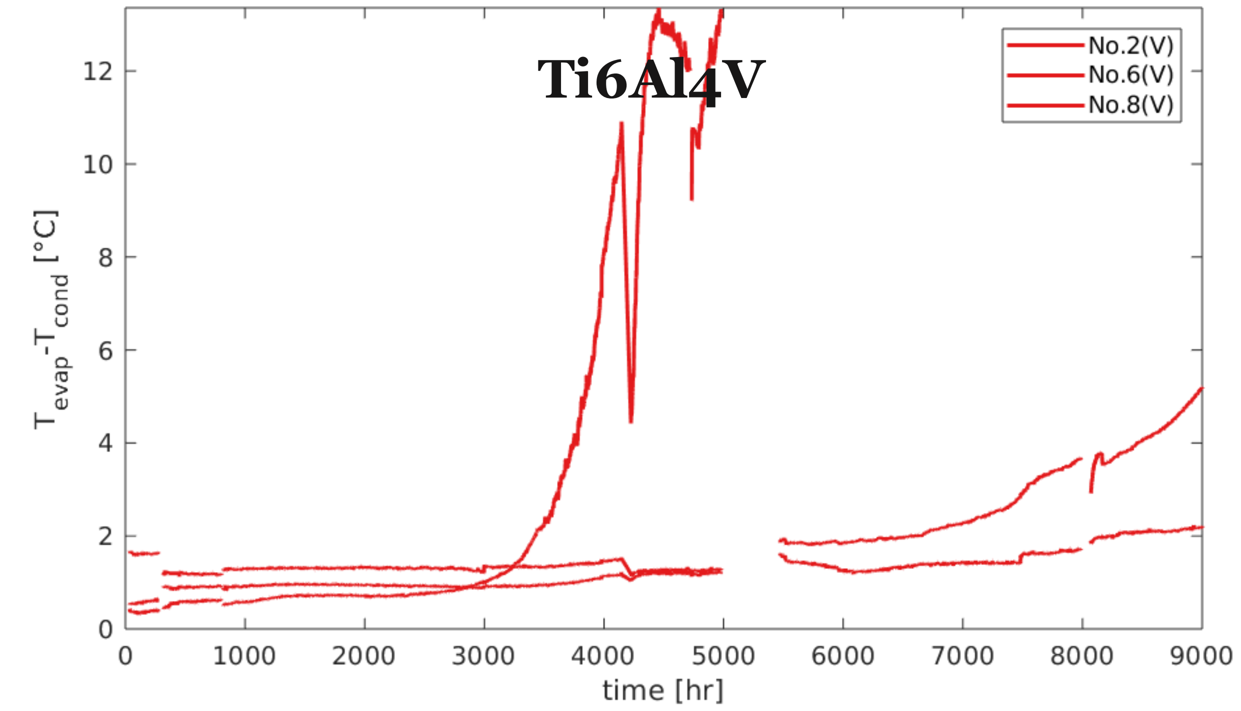


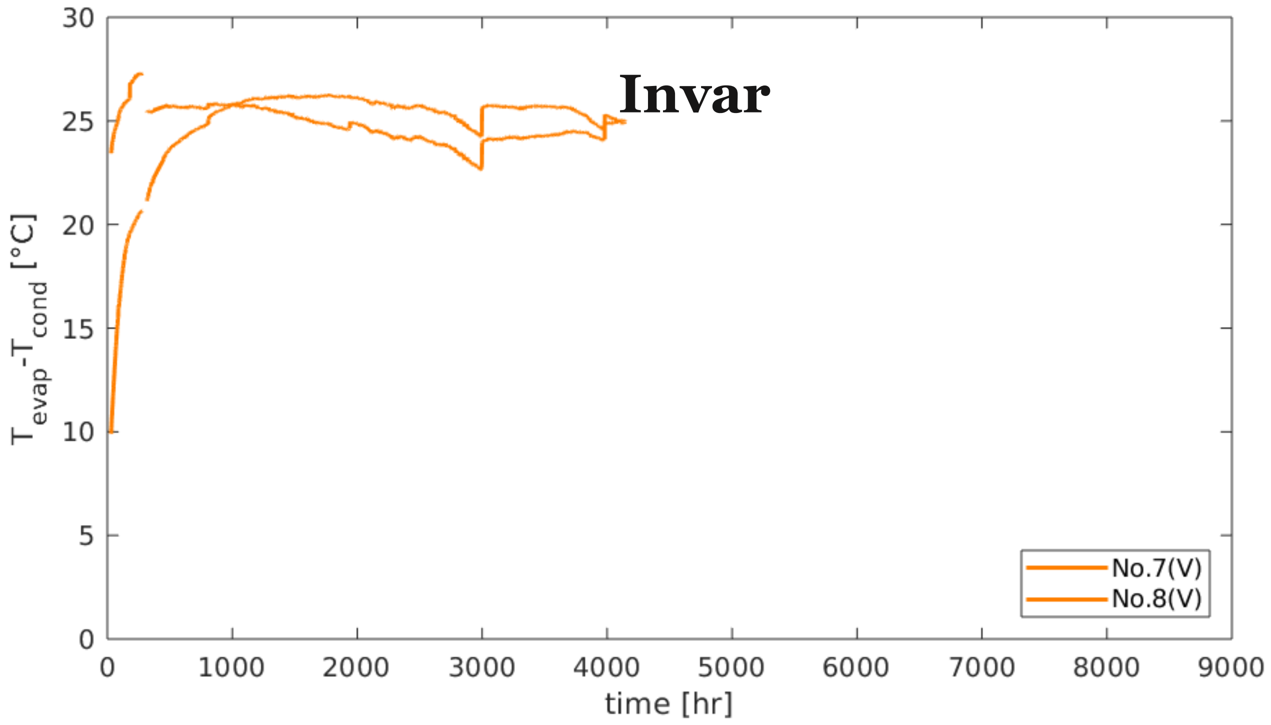
UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

WP4 Characterisation

- **Gas Plug Test - Methanol**







Some interaction with valve suspected

WP4 Characterisation

- **GC - Methanol**
  - Invar samples removed from gas plug at 4000 hours and re-weighed.

Sample No.	Mass of fluid fill [g]	Mass after filling [g]	Mass after 4000 hr [g]	dMass [g]
Invar 1	1.18	159.94	159.65	0.29
Invar 4	1.22	159.85	159.44	0.41

  - Small drop in mass so indicates possible NCG.
  - Gases detected:

Metal		**Gases detected [ppm]**				
		CH_4	**CO**	**CO_2**	**H_2**	**N_2**
ALM	Invar	793	14842	932	78062	49828

  - => Working fluid impurity level, *f* of 27981 ppm.

WP4 Characterisation

- **Sectioning - Methanol**
  - Invar sample cut at evaporator with pipe cutter and carefully sectioned.
  - Significant amount of loose green material found almost filling evaporator.

Evaporator
Liquid zone

Evaporator
L.-V. interface zone

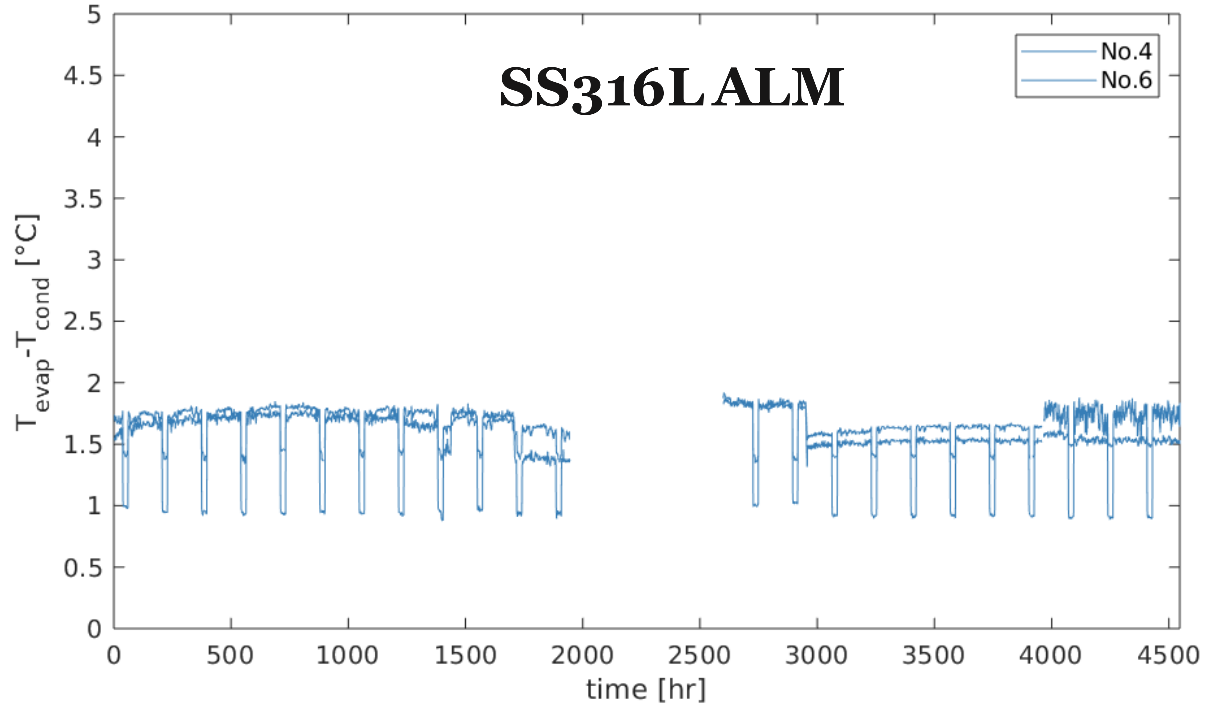
Green powder

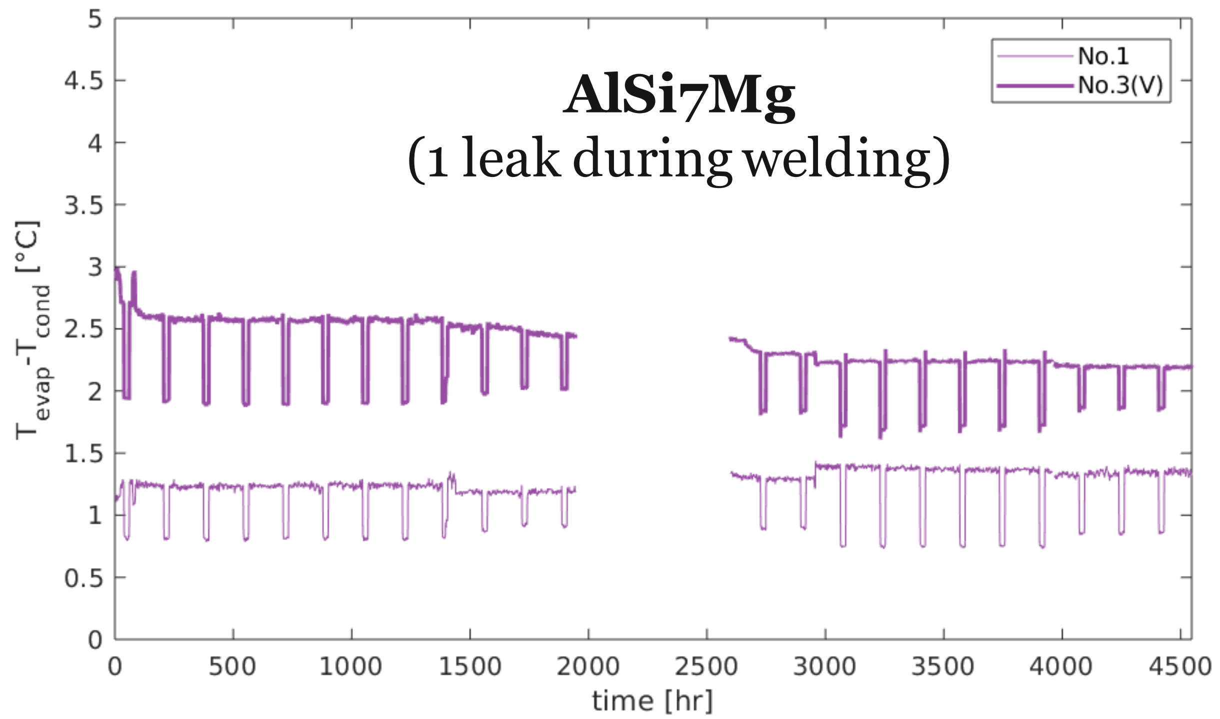
Condenser

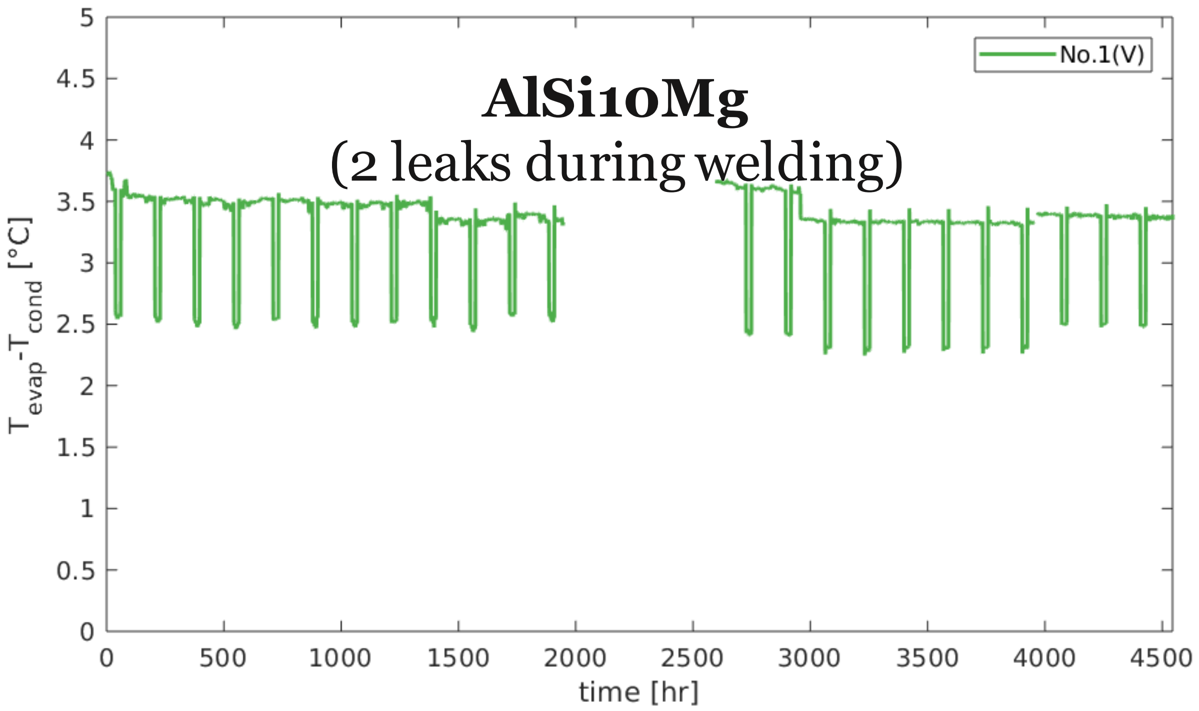
- From literature, nickel acts as a catalyst for methanol decomposition to produce CO and H_2.
- Green powder is consistent with NiO, the principal oxide of Ni.

WP4 Characterisation

- **Gas Plug Test - Propylene**



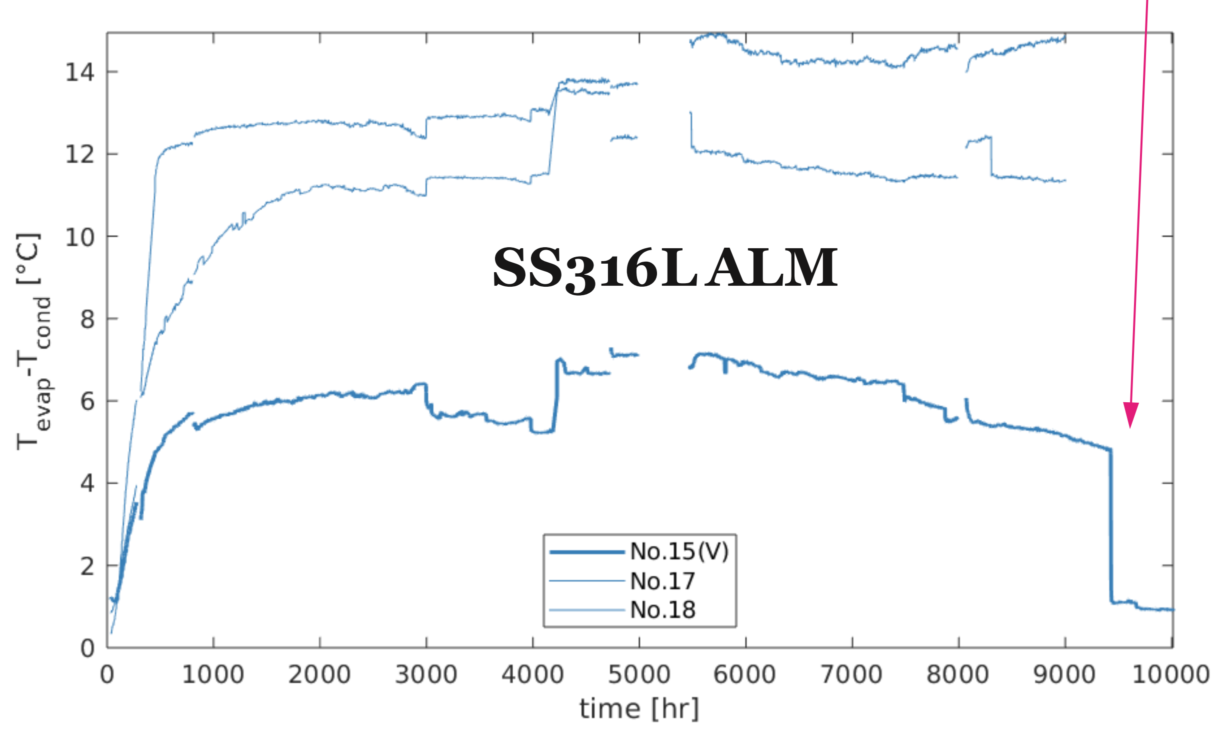


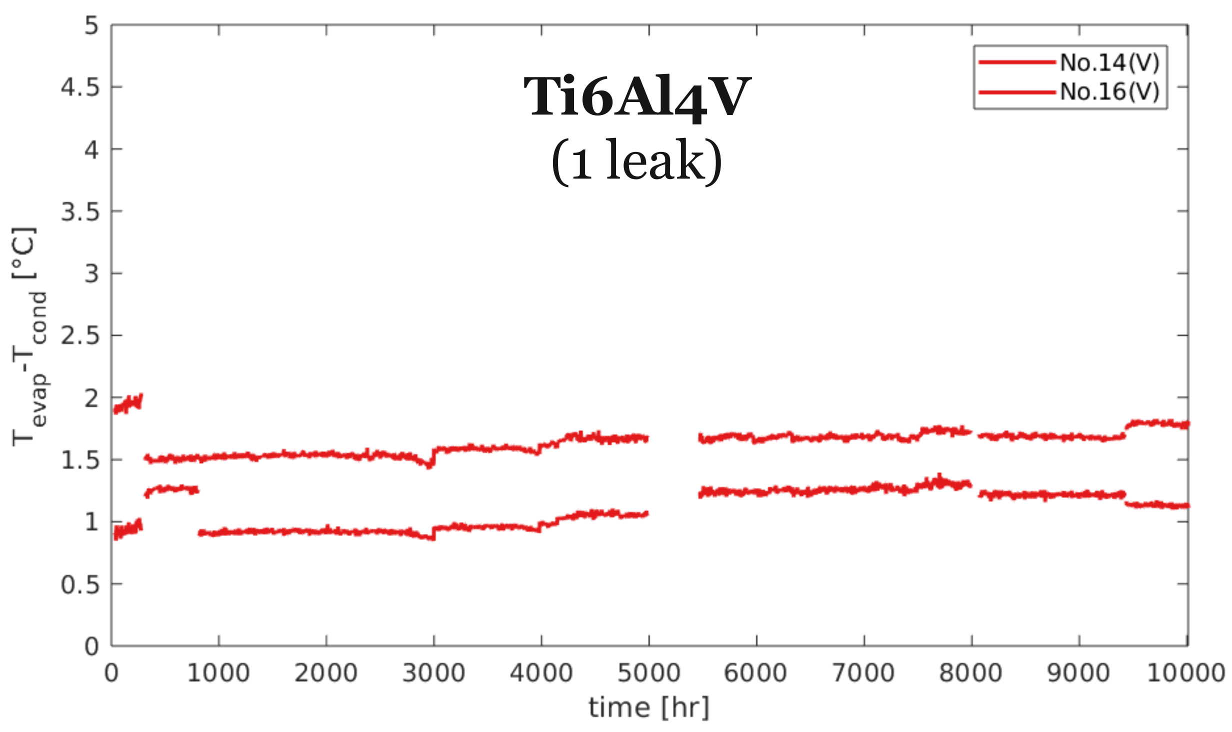


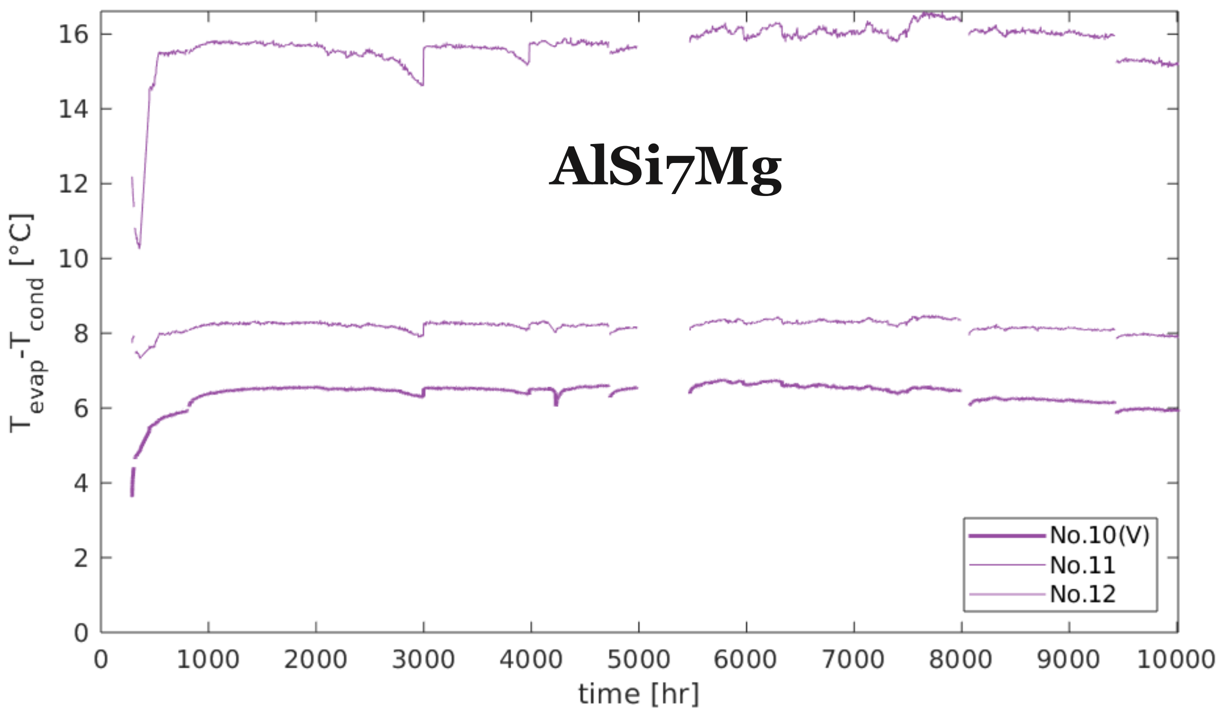
WP4 Characterisation

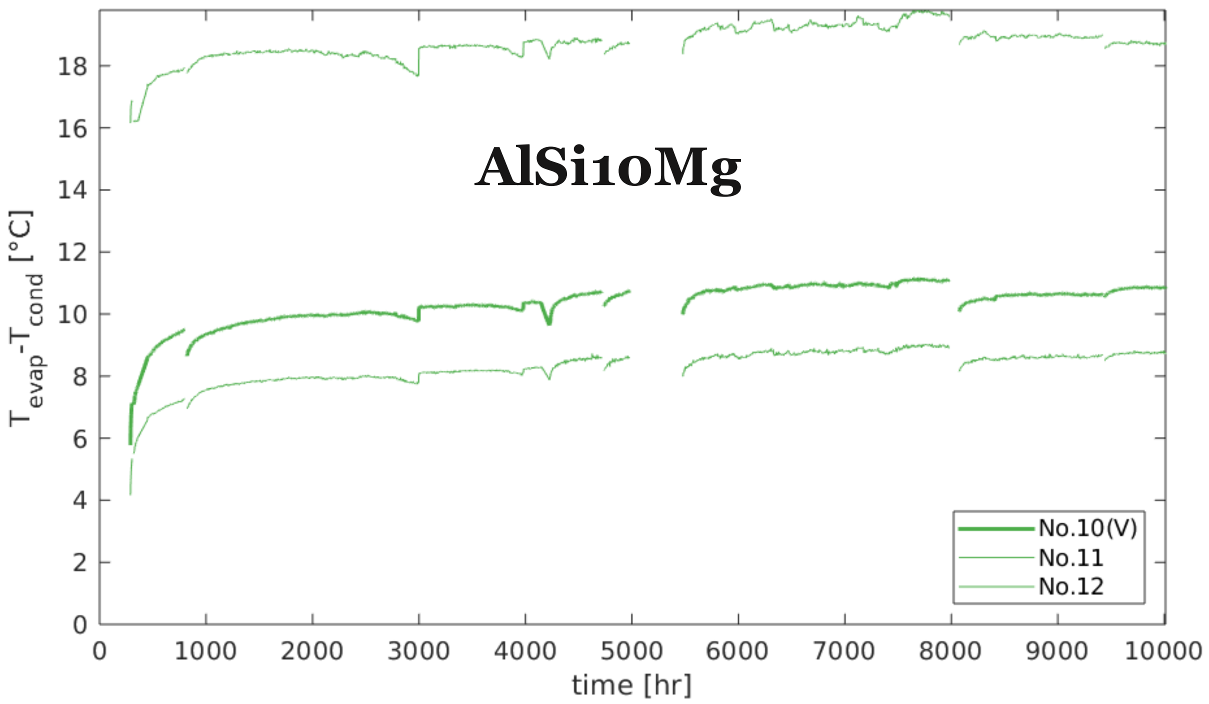
- **Gas Plug Test - Toluene**

Burped 'in-situ'



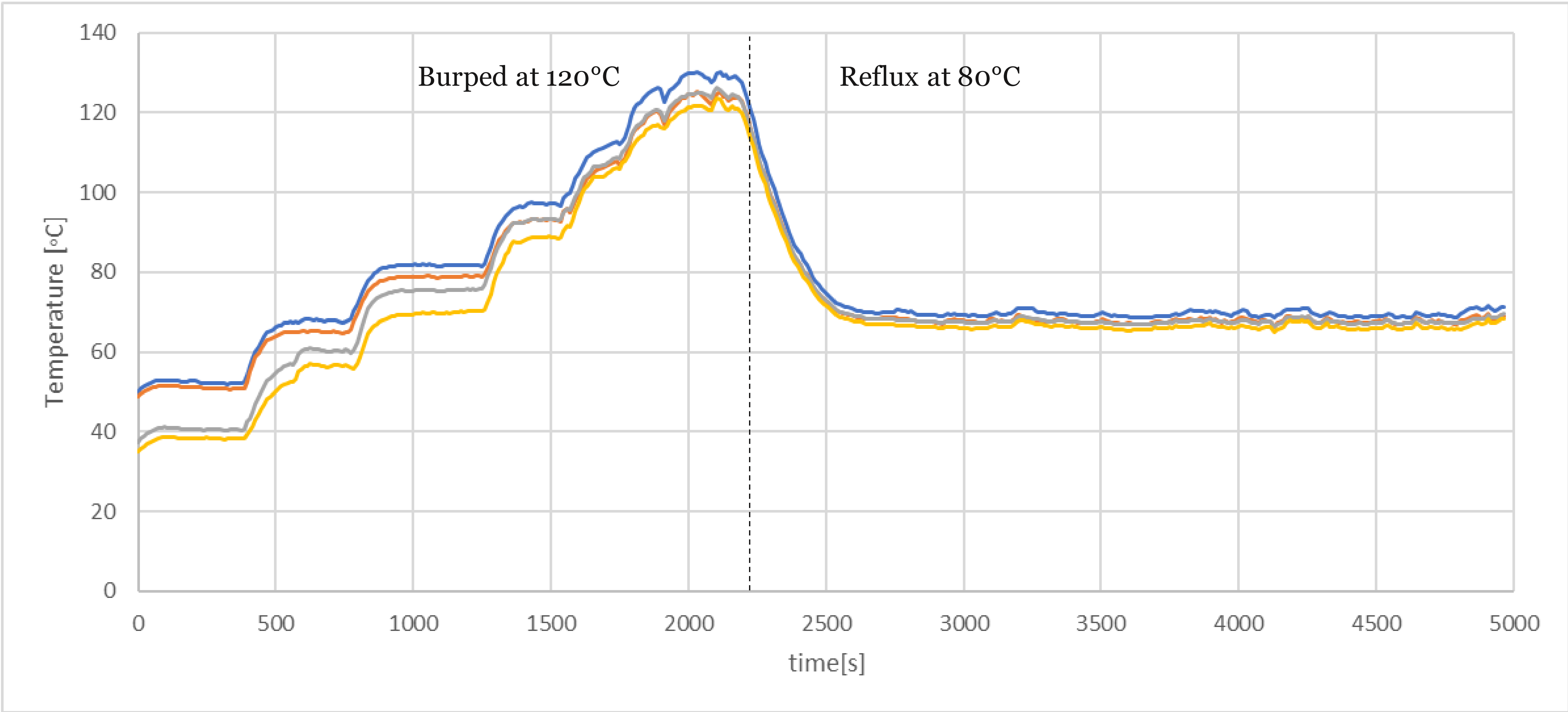






WP4 Characterisation

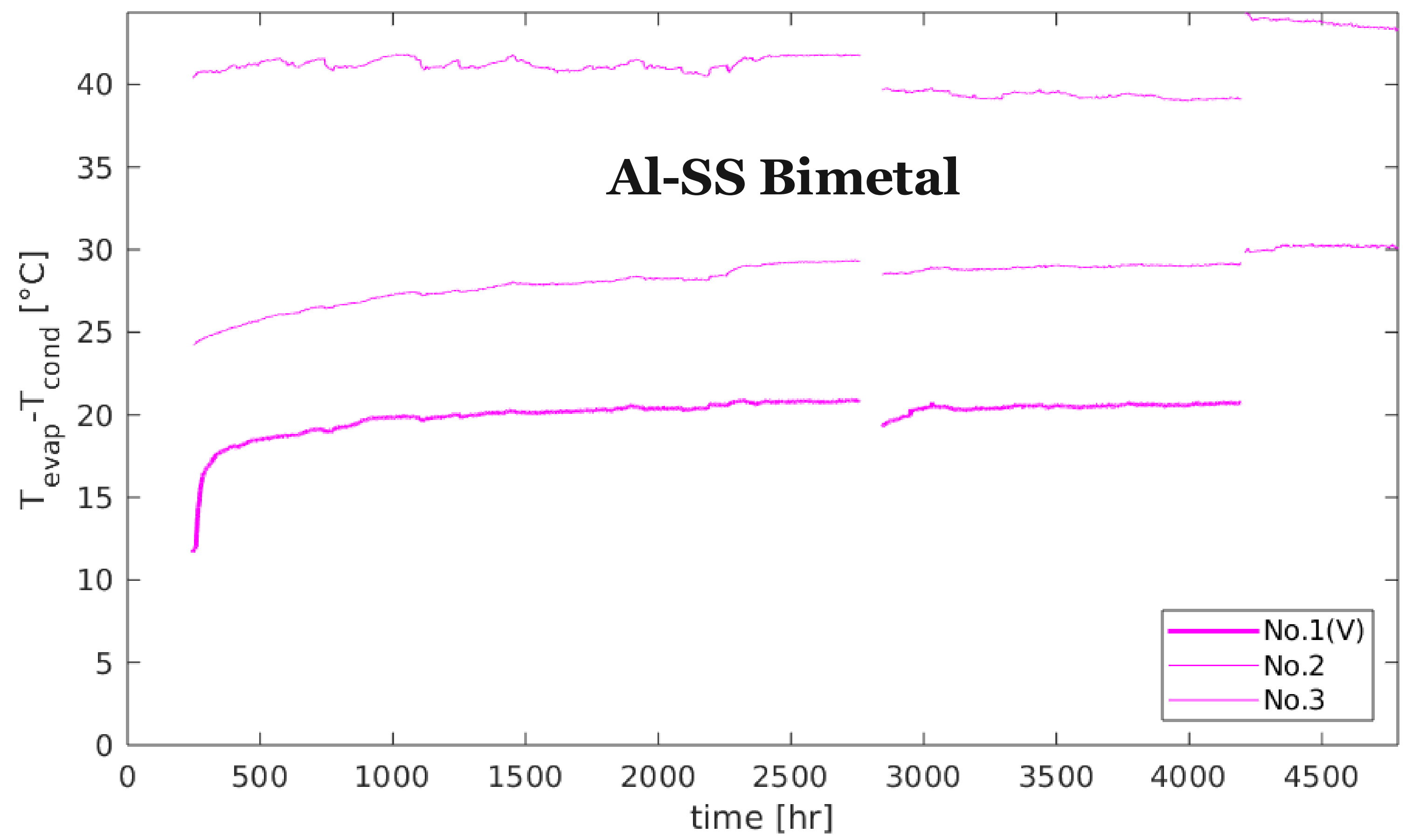
- **Gas Plug Test - Toluene**
  - AlSi7Mg removed from rig for burping in lab.



Still running 200 hrs later with ΔT = 1.8°C

WP4 Characterisation

- **Gas Plug Test - Toluene**



WP4 Characterisation

- **GC - Toluene**
  - Al-SS samples removed from gas plug at 4000 hours and re-weighed.

Sample No.	Mass of fluid fill [g]	Mass after filling [g]	Mass after 4000 hr [g]	dMass [g]
Al-SS 1	3.04	224.65	224.57	0.08

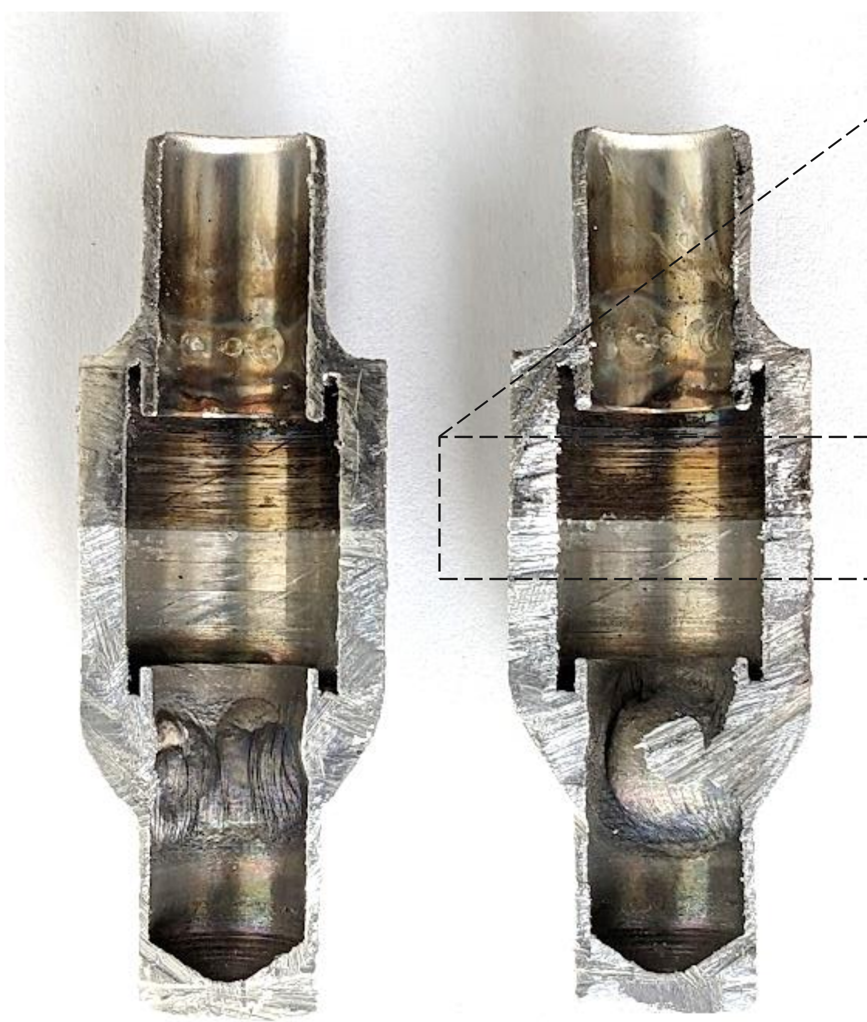
  - Small drop in mass so indicates possible NCG.
  - Gases detected:

Metal		**Gases detected [ppm]**				
		CH_4	**CO**	**CO_2**	**H_2**	**N_2**
Bimetal	Al-SS	96	2677	828	8092	16438

  - => Working fluid impurity level, *f* of 3577 ppm.

WP4 Characterisation

- **Sectioning - Toluene**
  - Al-SS sample cut with pipe cutter at evaporator and condenser, and carefully sectioned.



Evaporator

Condenser

Working fluid

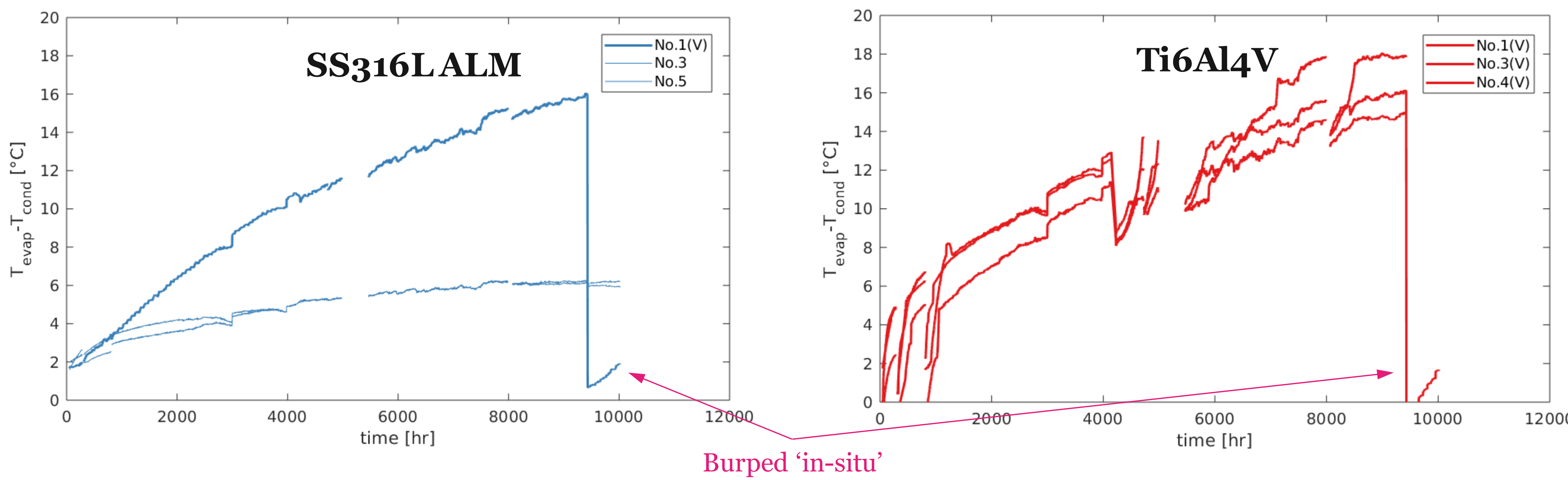
WP4 Characterisation

- **Sectioning - Toluene**
  - Clear weld colouration visible in evaporator.
  - No weld colouration visible in condenser (orbitally welded).
  - White zones in Al – SS coupling joint indicative of galvanic corrosion.
  - Awaiting XPS results.

UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

WP4 Characterisation

- **Gas Plug Test – Water**



  - Continuous increase in ΔT over 9000 hours.
  - After burp for each material, still see increase in ΔT over time.

WP4 Characterisation

- **Sectioning/XPS – Water**
  - SS316L sample cut at evaporator with pipe cutter and carefully sectioned.
  - XPS identified:
    - For green zone, mainly $Ni(OH)_2$, Fe_2O_3 and some Cr_2O_3.
    - For red zone, mainly Fe_2O_3 with no chromium layer.

SS316L ALM
Light green colour in liquid region.
Orange colour in L.V. region.

Water
Clear but contained a significant amount of loose particles.

WP4 Characterisation

- **Sectioning/XPS – Water**
  - Different sources in literature list SS316L as either compatible or incompatible as it is known to continuously produce H_2.
  - This has been found to be a function of the alloy composition, temperature, surface condition and fluid purity.
  - Even for “harmless” high purity de-ionised and de-oxygenated water with a neutral pH of 7, corrosion of passivated 316L stainless steel surfaces takes place, and is an ongoing problem, particularly in the pharmaceutical industry.
  - In most cases reaction is:

$$Fe + H_2O \rightarrow Fe(OH)_2 + H_2$$

  - In oxygen free environments, this iron hydroxide can be oxidised by reaction with water:

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O + H_2$$

  - Alternatively, water molecules oxidise iron along the grain boundaries despite the presence of a protective chromium based passivating layer:

$$2Fe^0 + 3H_2O \rightarrow Fe_2O_3 + 3H_2$$

WP4 Characterisation

- **Sectioning/XPS – Water**
  - Ti6Al4V sample cut at evaporator with pipe cutter and carefully sectioned.
  - XPS identified:
    - Mainly oxides of TiO_2 and Al_2O_3.
  - As valve is SS316L, it was also disassembled but no obvious traces of oxidation were found.

Ti6Al4V
Orange colour in liquid region.

Water
Orange tint and contained some loose particles.

WP4 Characterisation

- **Sectioning/XPS – Water**
  - One example of Ti Grade 5 - water heat pipes in literature which has undertaken life tests [*Anderson, 2013*].
  - Has run successfully at 270°C for 40,000 hours, but details are not available for corrosion analysis, cleaning or burping.
  - Noted that rough surface Ti CP wire wicks showed a larger reactive layer compared to smooth tubing.

  - Further study required for water combinations.

WP4 Characterisation

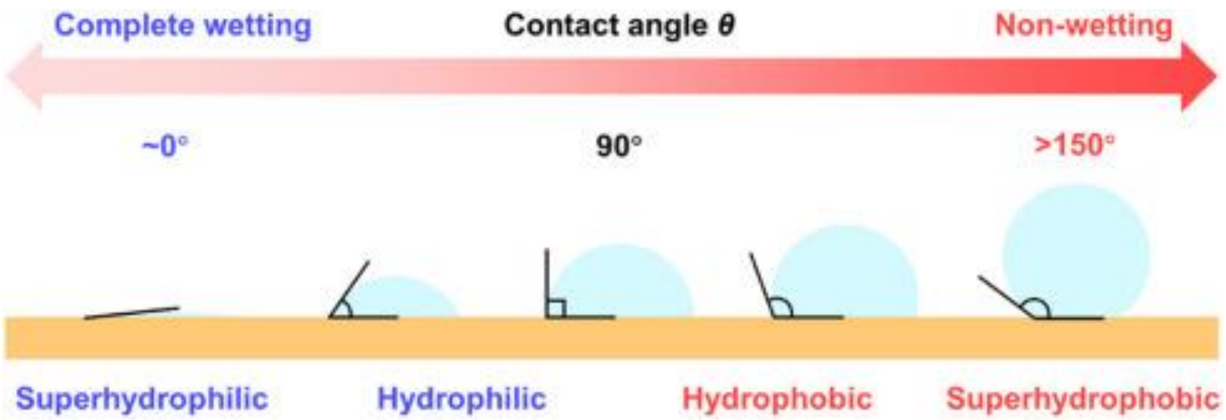
- **NCG and Corrosion Analysis Summary**

	ALM					SCouP			Conventional		Bimetal.
	SS316L	**Ti6Al4V**	**Invar**	**AlSi10Mg**	**AlSi7Mg**	**SS316L**	**AlSi10Mg**	**AlSi7Mg**	**SS316L**	**Al6061**	
Acetone											
Ammonia											
E. Glycol											
Methanol											
Propylene											
Toluene											
Water											

- Pending XPS and EDX results to be included in final report.

WP4 Characterisation

- **Wettability**
  - Measurement of liquid-solid contact angle between working fluid and container/wick material.
  - For optimal heat transport, contact angle should be close to zero, or at least very small.



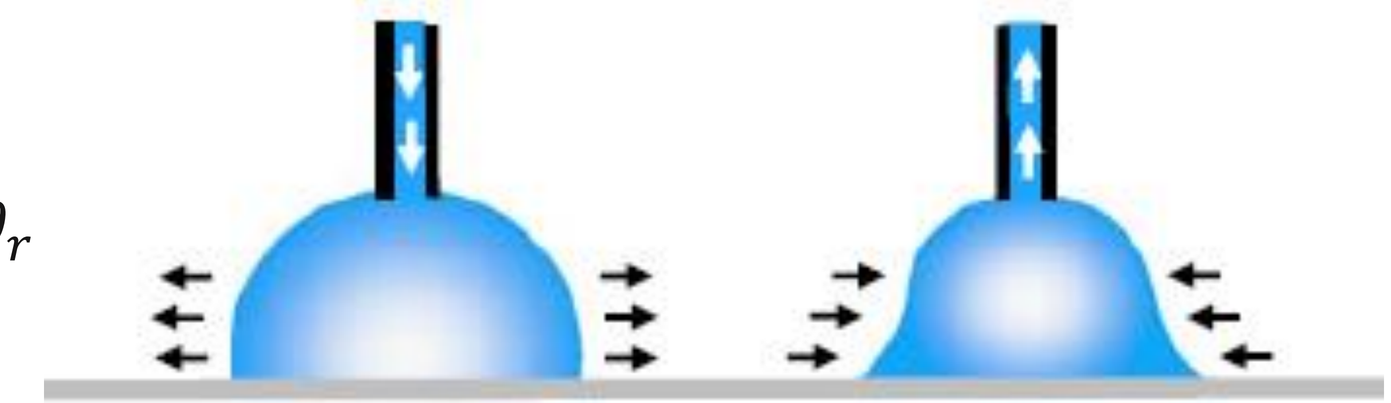
[Song & Fan, 2021]

  - Measurement of droplet contact angle requires fluid to be a liquid at STP.
  - For the case of cryogenic fluids and refrigerants, the approach used in literature is to measure the contact angle through the view ports of a pressure vessel.
  - For volatile liquids it is also preferable to perform contact angle measurements inside an enclosed chamber to reduce the effects of evaporation.

WP4 Characterisation

- **Wettability**
  - Dynamic contact is generally of more interest to characterise wetting where the contact line may be in motion.

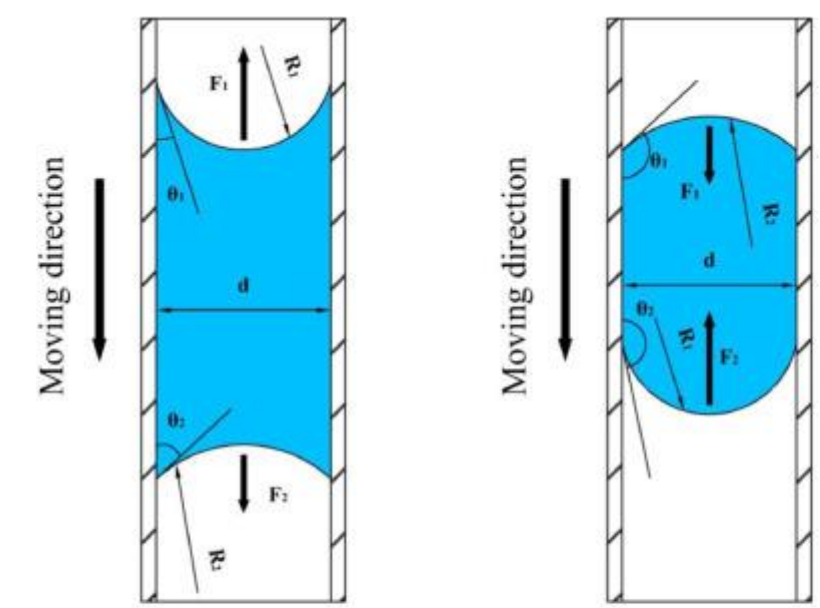
$$H = \theta_a - \theta_r$$



Advancing contact angle　　Receding contact angle

  - Surface roughness plays a large role in generating hysteresis - the actual microscopic variations of slope on the surface create barriers that pin the motion of the contact line and alter the macroscopic contact angles.
  - For PHPs, dynamic contact angle hysteresis is directly related to capillary resistance:

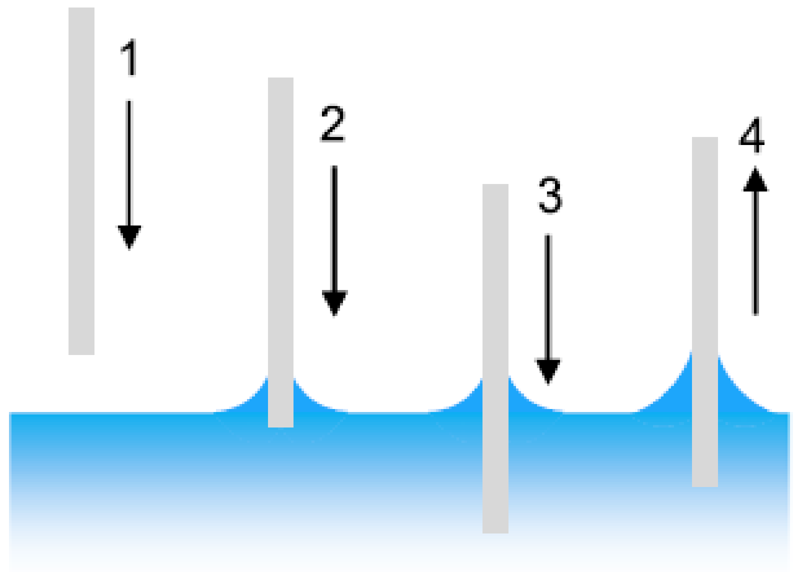
$$F_{cap} = 2\pi r_{in}\sigma(\cos\theta_{advancing} - \cos\theta_{receding})$$



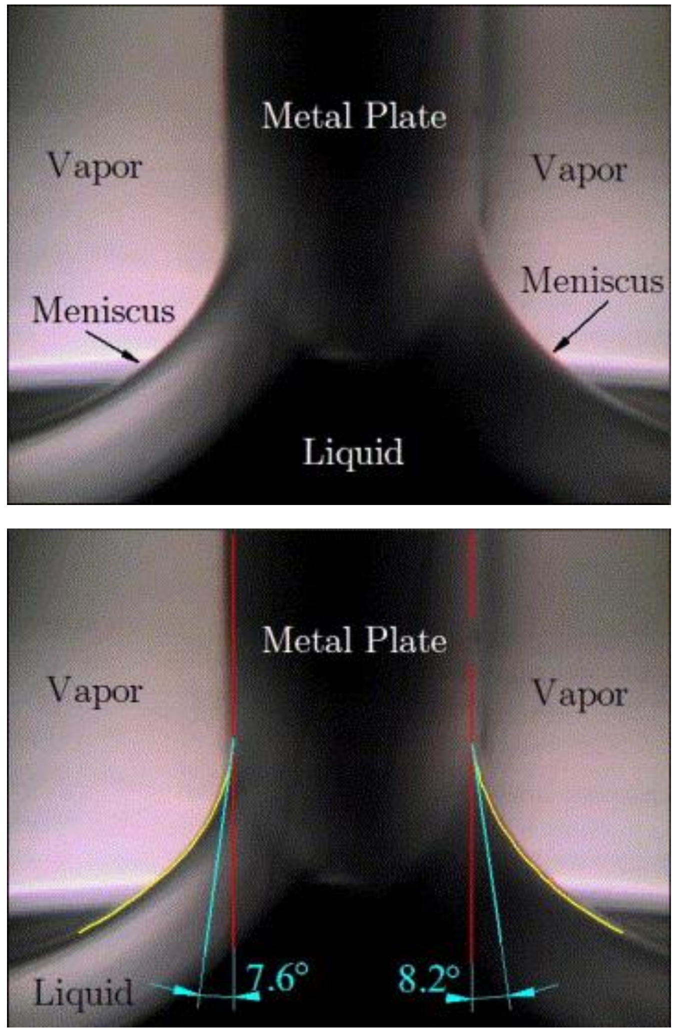
(a) Hydrophilic　　(b) Hydrophobic

WP4 Characterisation

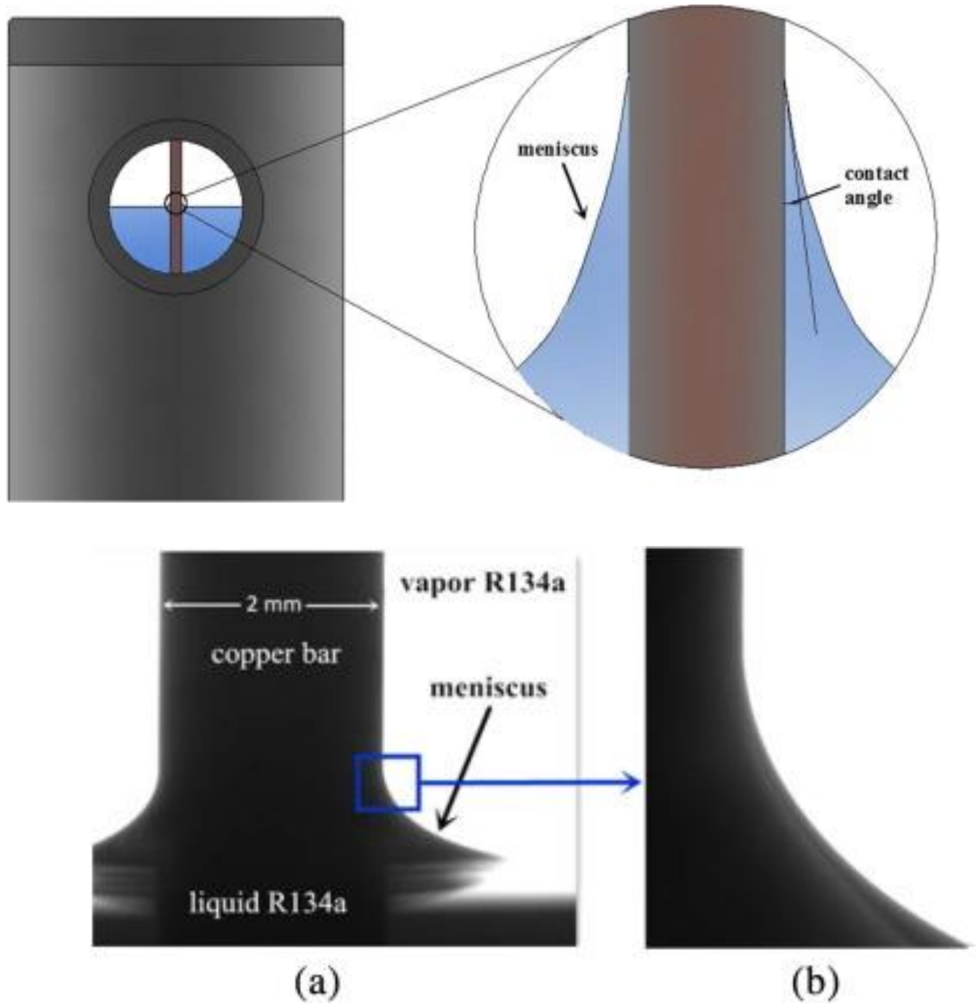
- **Wettability**
  - Wilhelmy plate method (ASTM D1331-20), with modifications.



Submersion cycle for the Wilhelmy balance method (ASTM D1331-20)



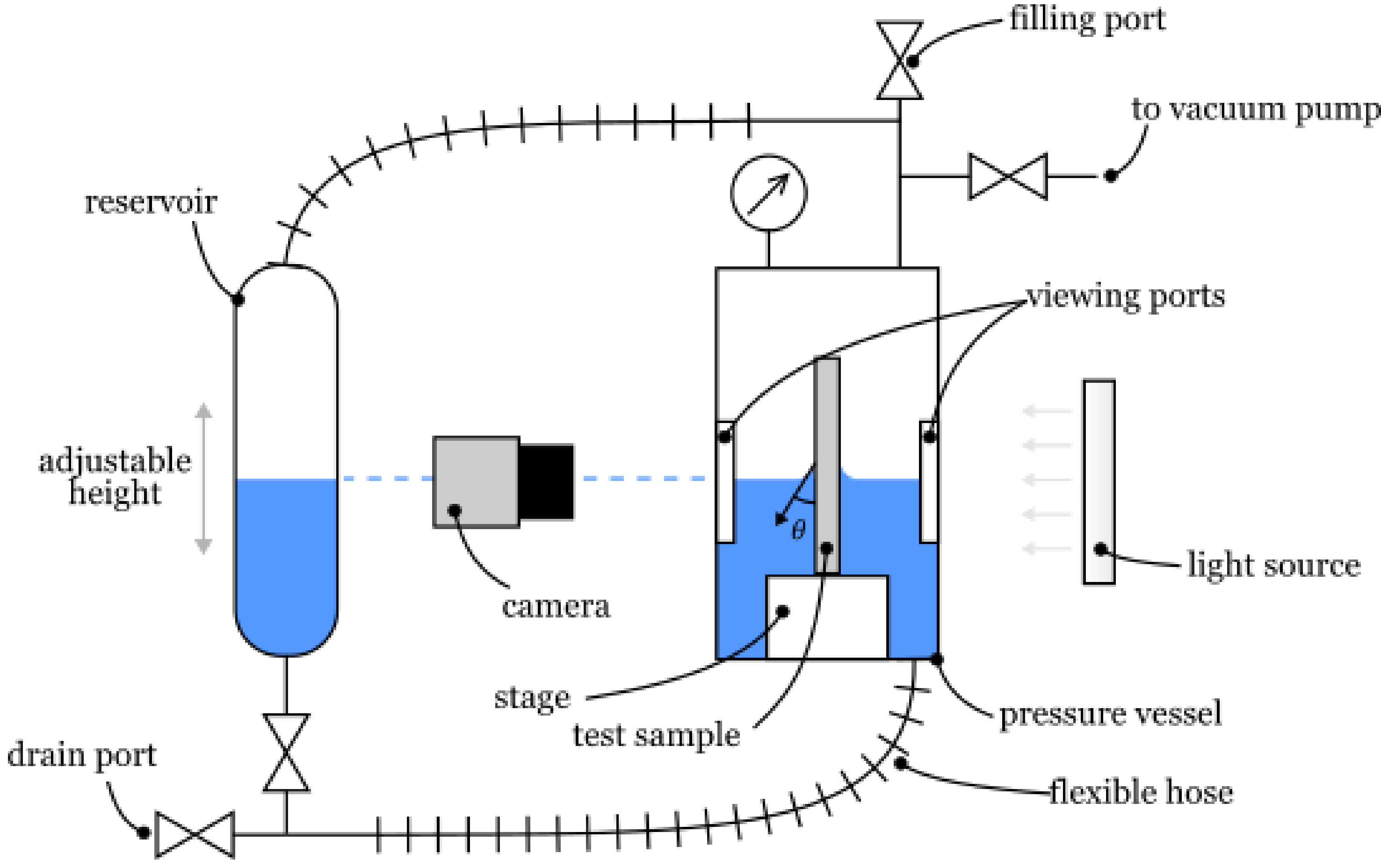
[Vadgama and Harris, 2007, Exp. Therm. Fluid Sci., 31, pp. 979-984.]



[Lu et al., 2016, Int. J. Heat Mass Transf., 102, pp. 877-883.]

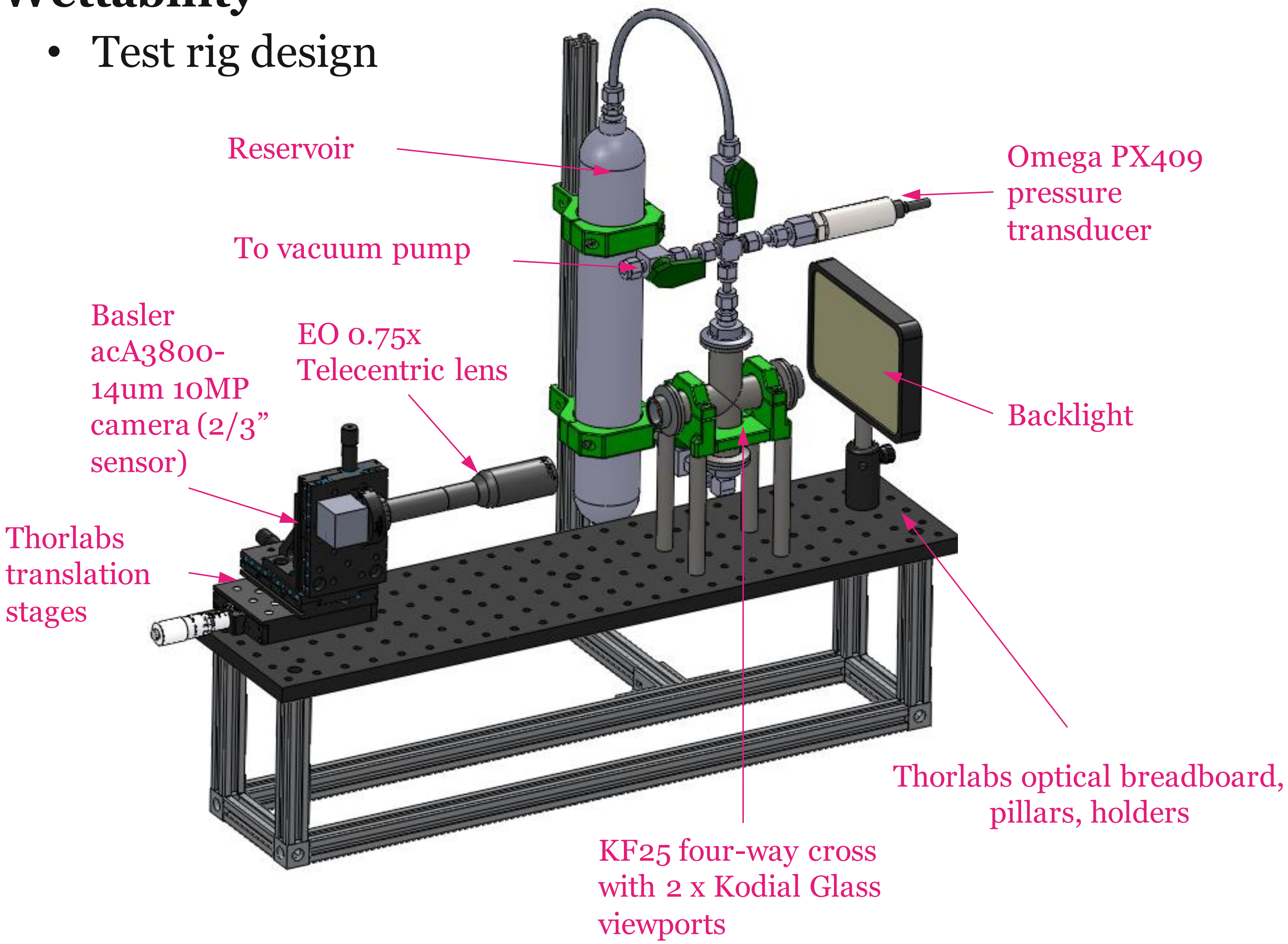
WP4 Characterisation

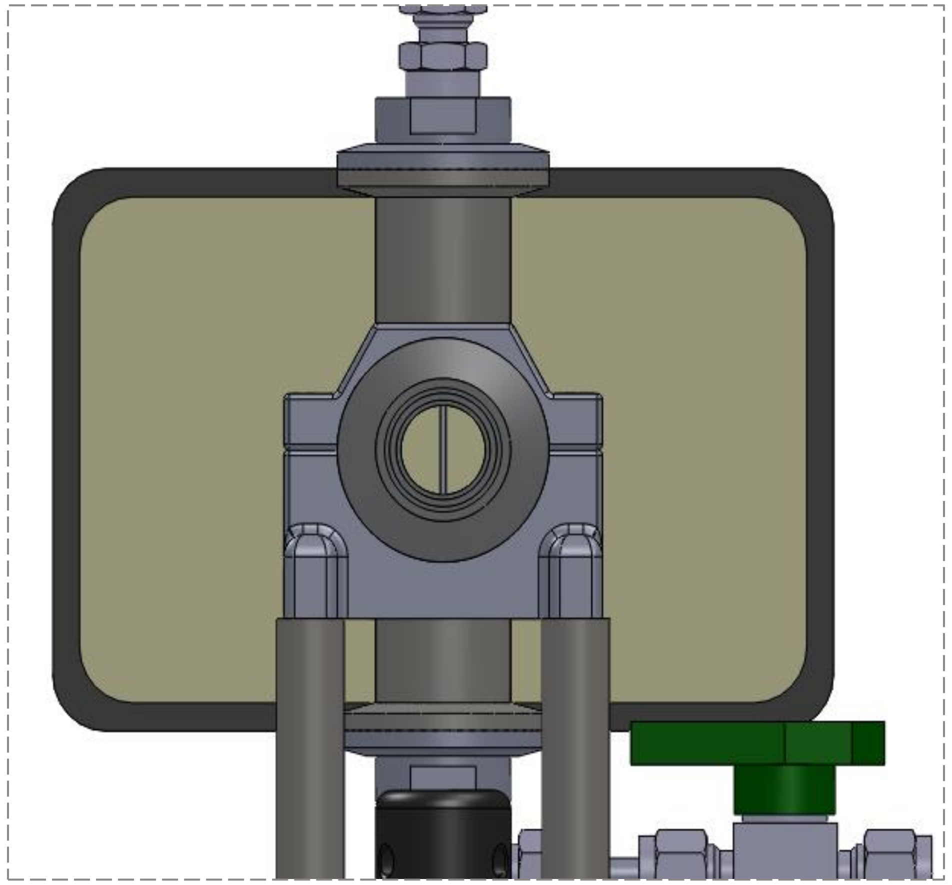
- **Wettability**
  - Test rig design
    - Pressure vessel with optical viewport for camera and back light source.
    - For liquid working fluids, they are added through filling port up to height of viewing port.
    - Connection to vacuum pump (via. cold trap) to remove air and have single species environment.
    - Pressure monitored by Omega PX309-300A5V transducer.
    - Reservoir allows for adjusting the height and direction of flow of liquid-vapour interface for contact angle hysteresis measurements.
    - For gases, sufficient volume of fluid will be condensed inside the reservoir from gas supply tank.



WP4 Characterisation

- **Wettability**
  - Test rig design

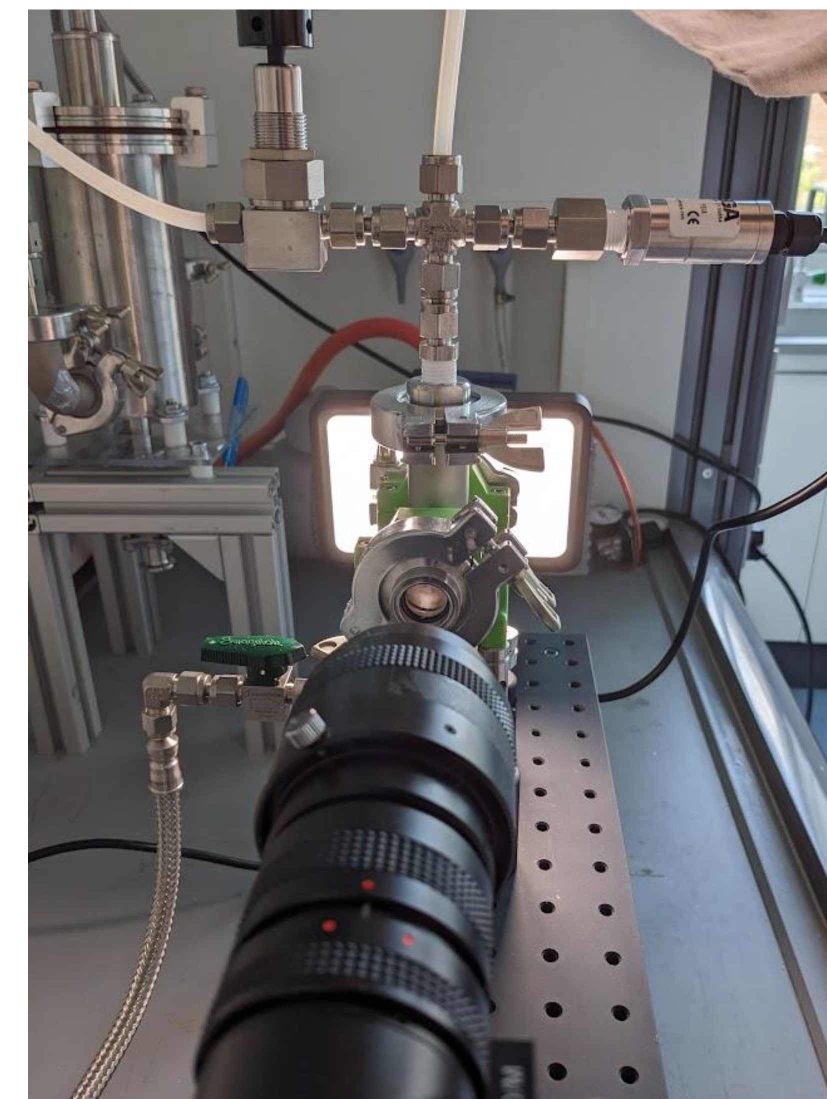




Side View

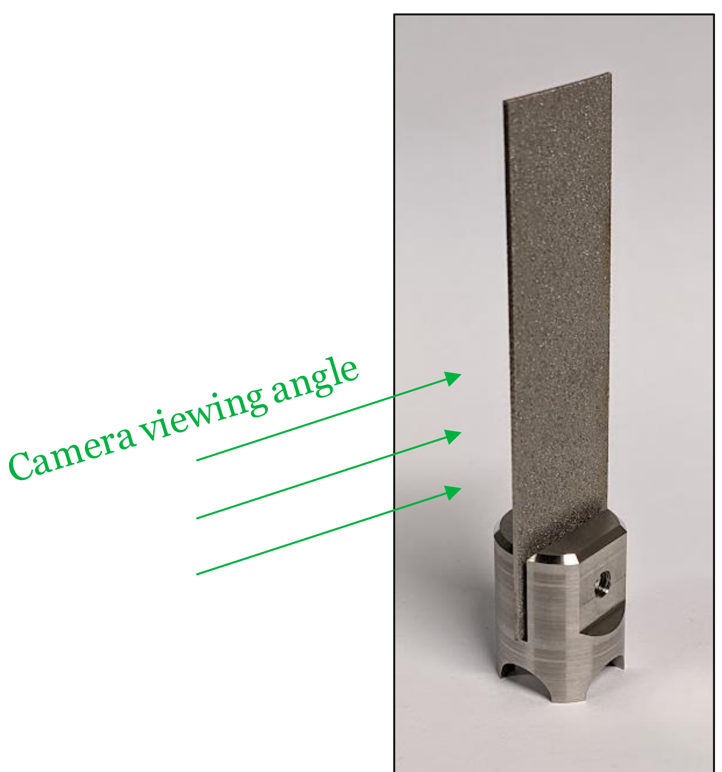
WP4 Characterisation

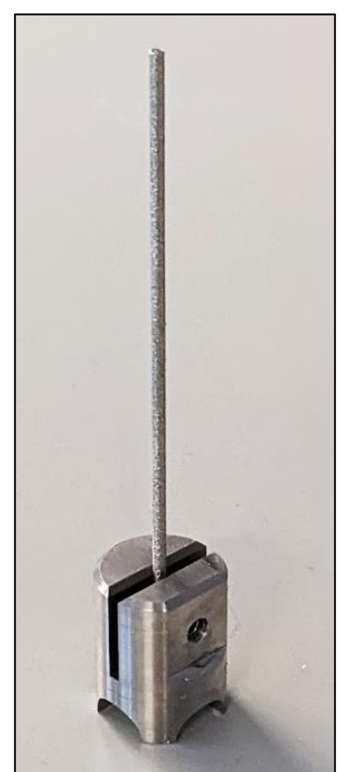
- **Wettability**
    - Test rig design

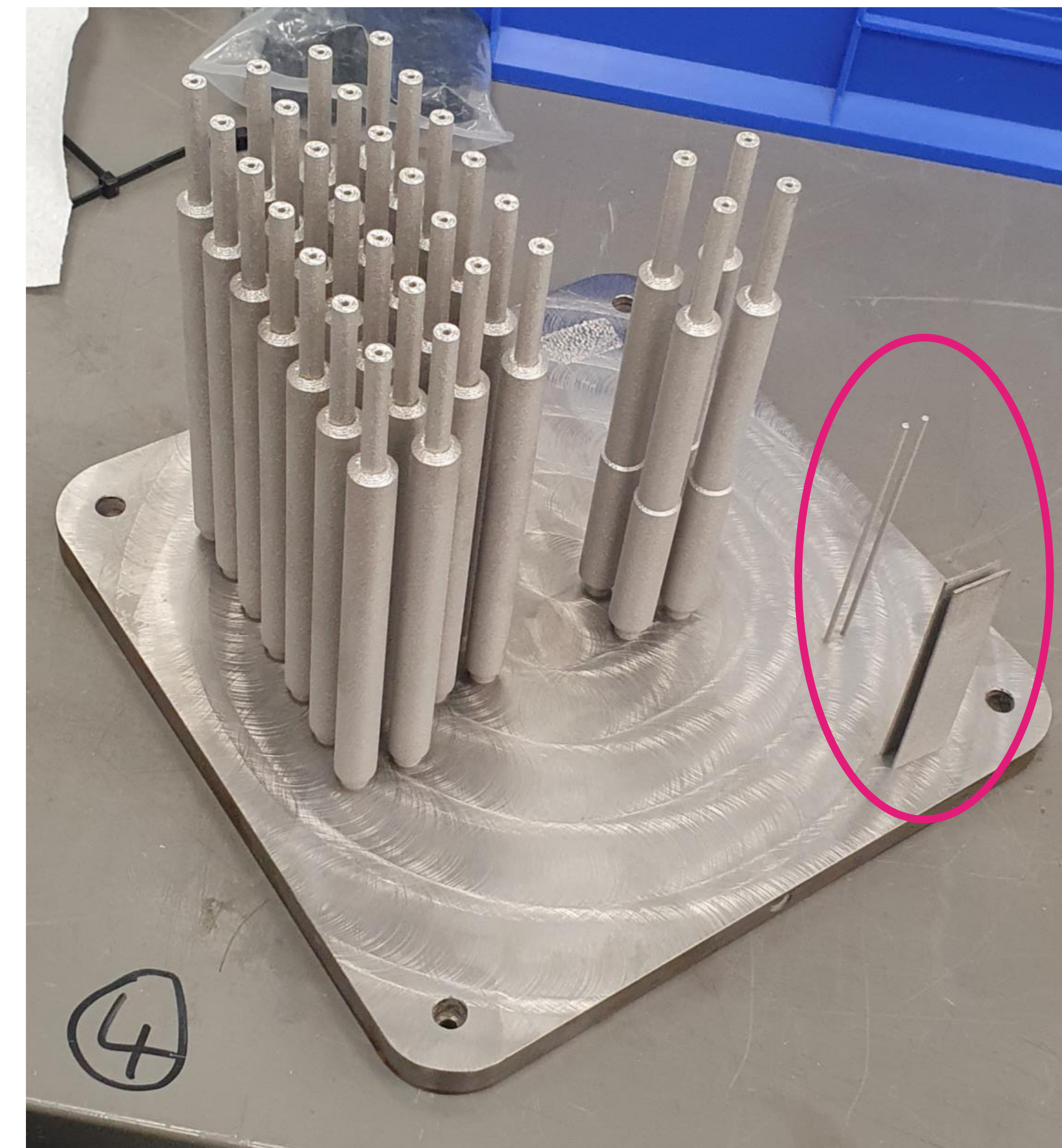


WP4 Characterisation

- **Wettability**
  - 2 different style ALM coupons for each material were printed at same time as thermosyphons:
    - Rectangle 80 x 20 x 1 mm (H x W x D)
    - Cylinder 100 x 2 mm (H x OD)
  - Tested in ‘as-built’ condition.
  - SS316L machined sample holders for pressure vessel:







SS316L

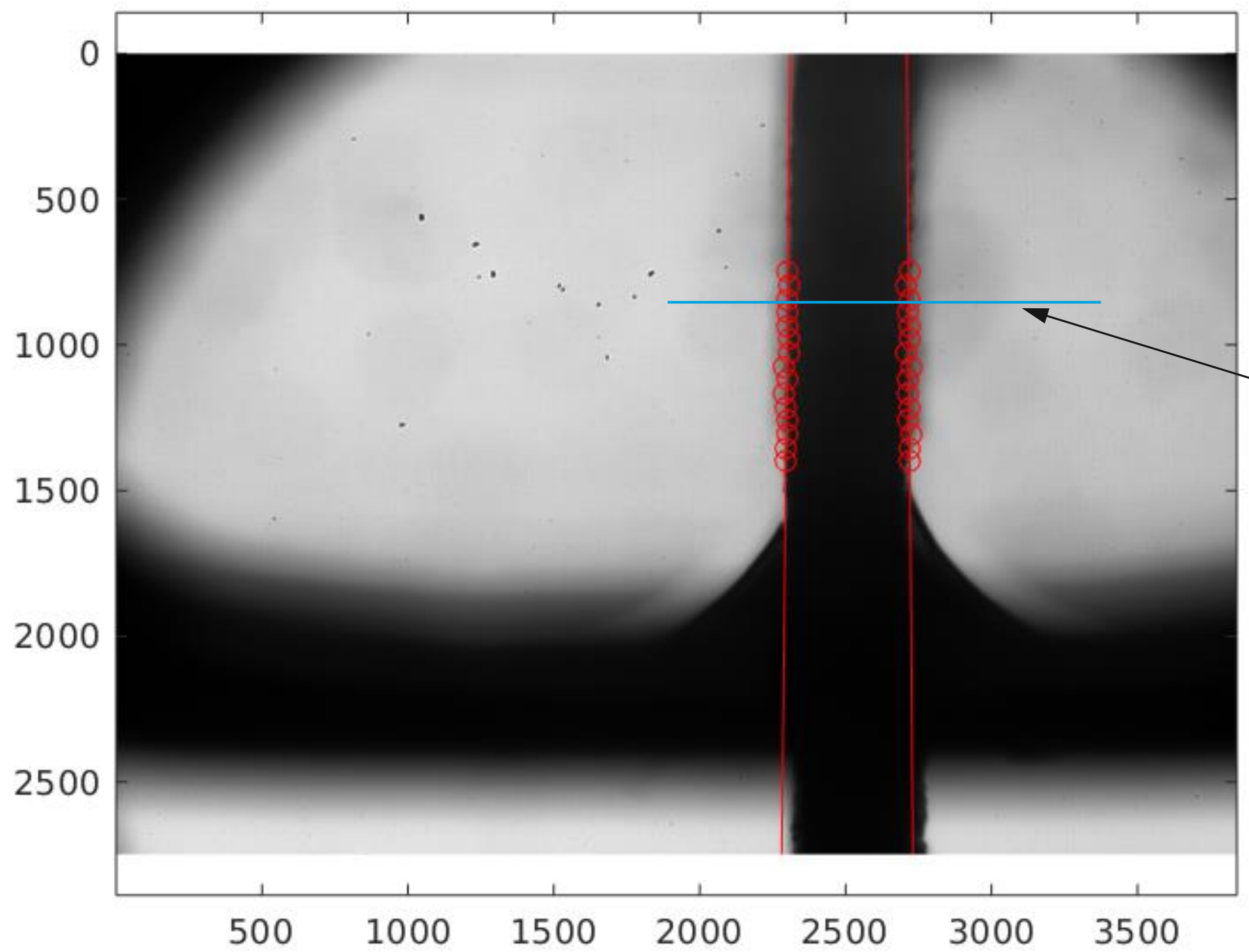
WP4 Characterisation

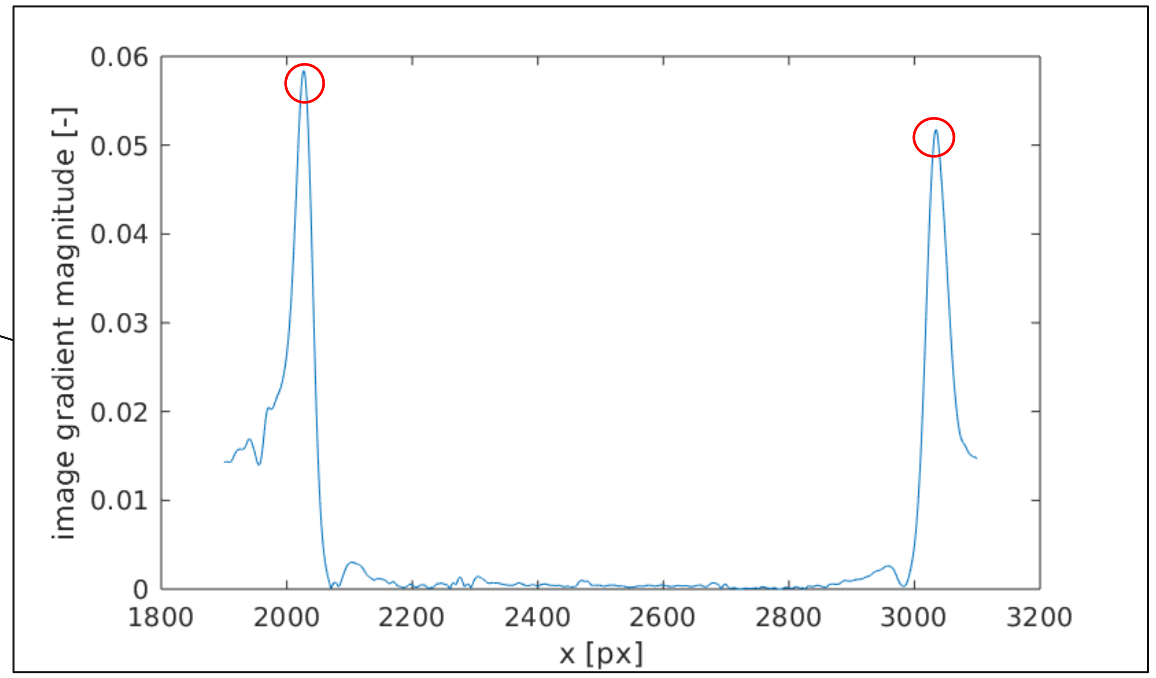
- **Wettability**
  - Acquisition of images (3840 x 2748 pixels).
  - Image processing with MATLAB.

Capture sequence of images

↓

Find sample vertical edges

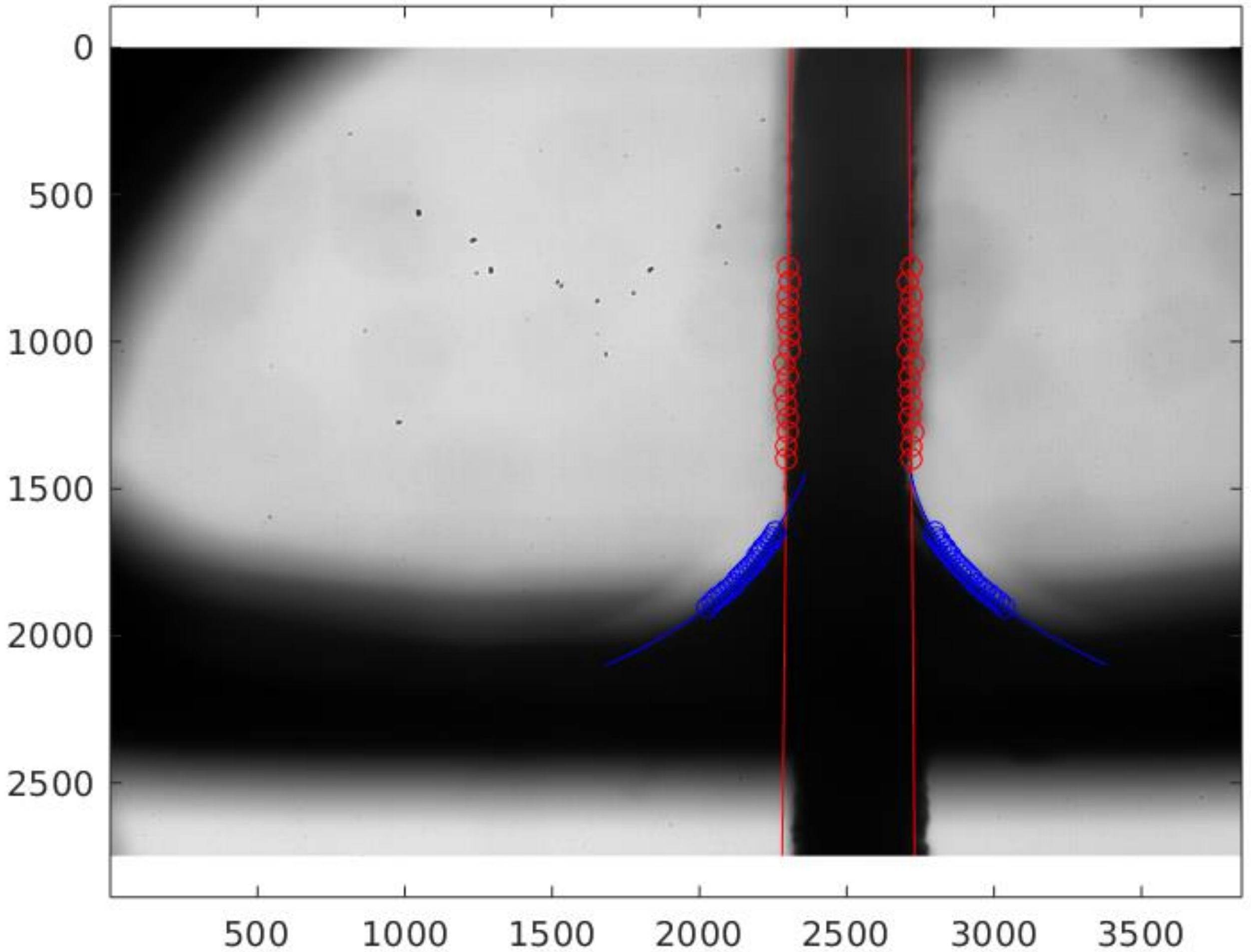


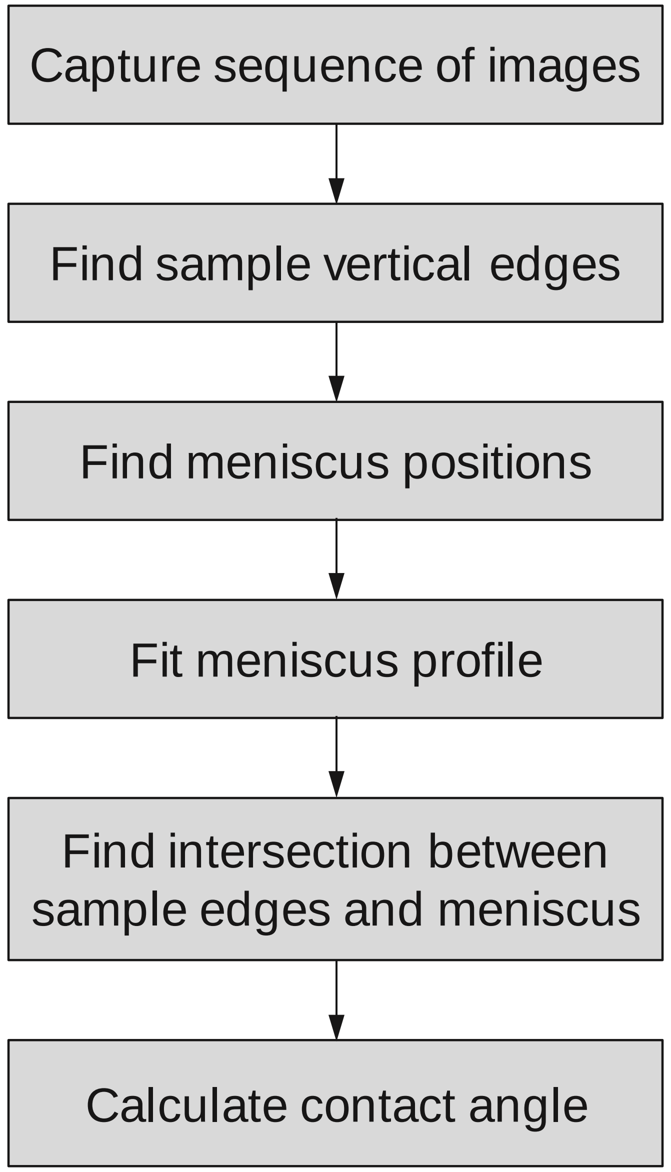


UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

WP4 Characterisation

- **Wettability**
  - Acquisition of images (3840 x 2748 pixels).
  - Image processing with MATLAB.



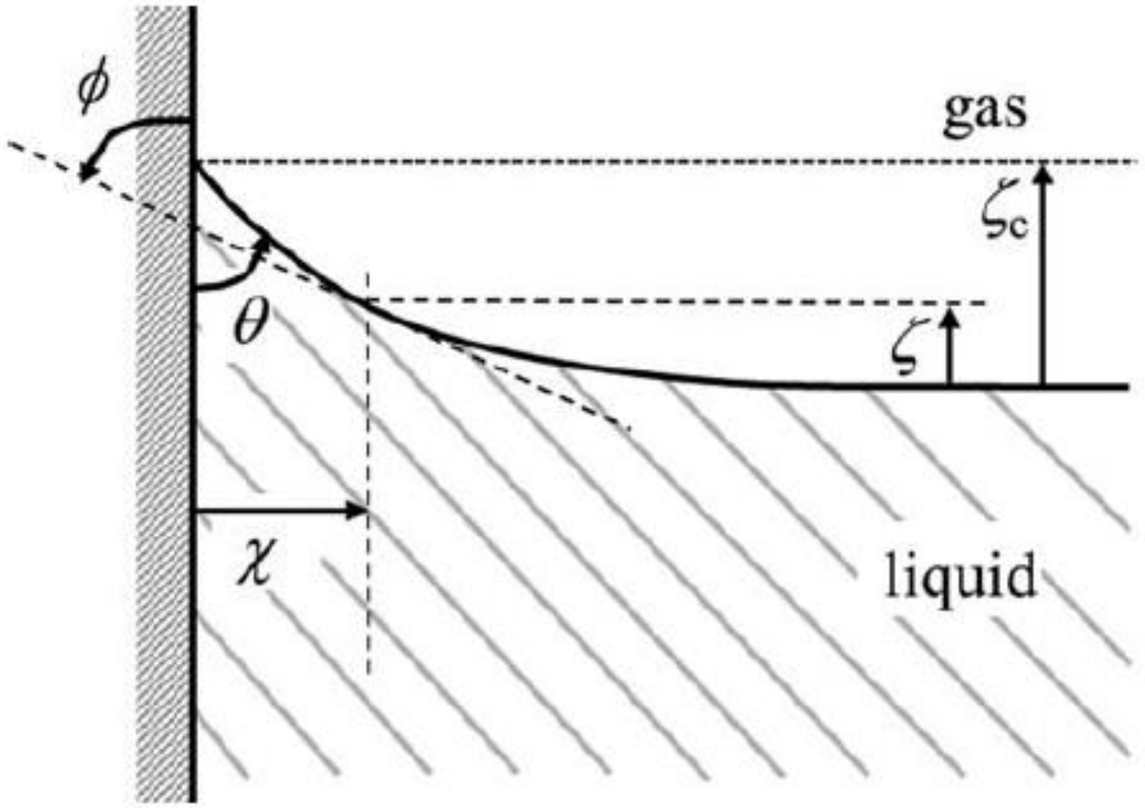


University of Limerick – Ollscoil Luimnigh | Bernal Institute

WP4 Characterisation

- **Wettability**
  - Meniscus at a single vertical wall [*deWijs et al., 2016*]:

$$\sin\phi = 1 - \frac{\rho_L g}{2\gamma}\zeta^2$$



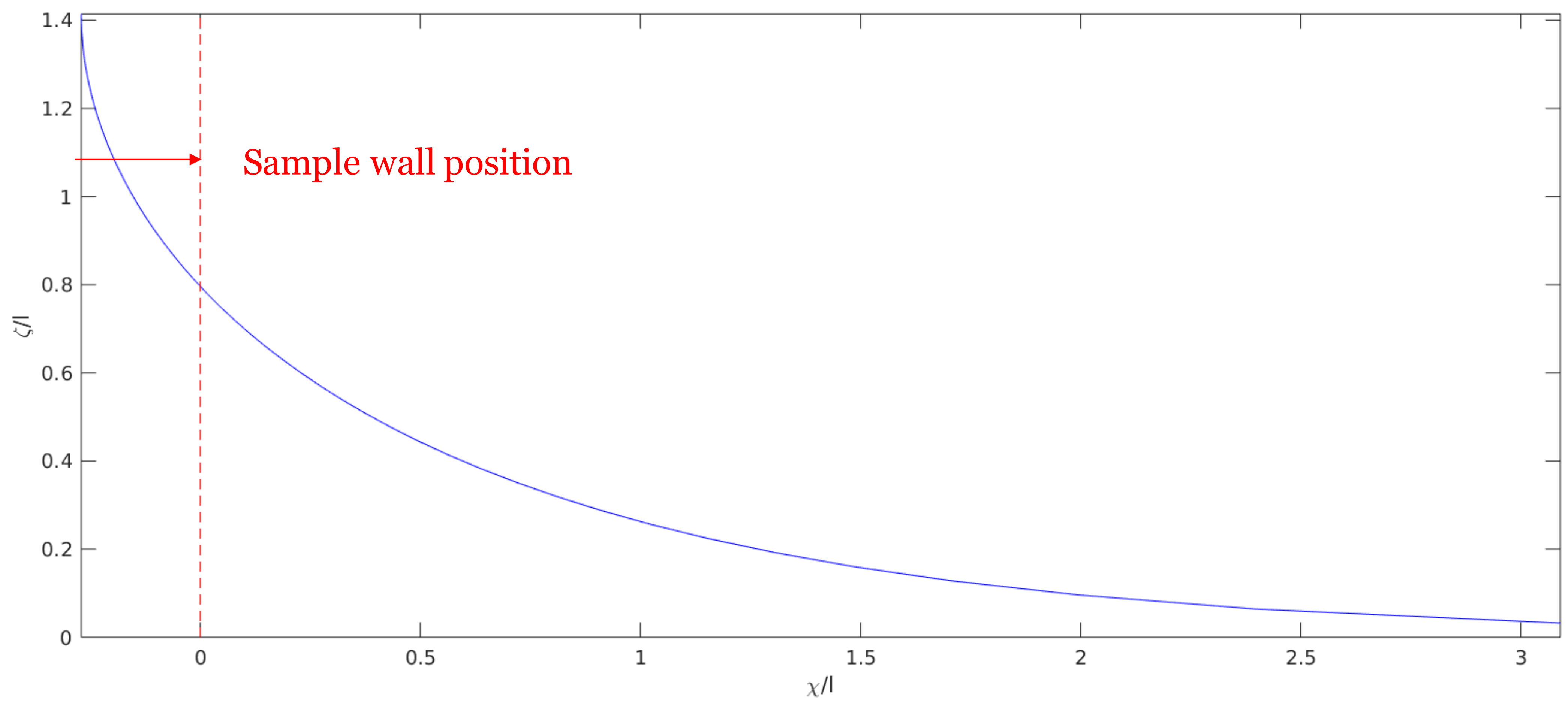
  - Capillary length, $l = \sqrt{2\gamma/\rho_L g}$
  - As $\phi \to 0$, $\zeta/l \longrightarrow \sqrt{2}$

  - $\zeta/l = 2l\ sin\left(\frac{\pi}{2} - \phi\right)$
  - $\chi/l = \log\frac{\frac{2l}{\zeta} - \sqrt{\left(\frac{2l}{\zeta}\right)^2 - 1}}{\sqrt{2}-1} - 2\sqrt{1 - \left(\frac{\zeta}{2l}\right)^2} + \sqrt{2}$

UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

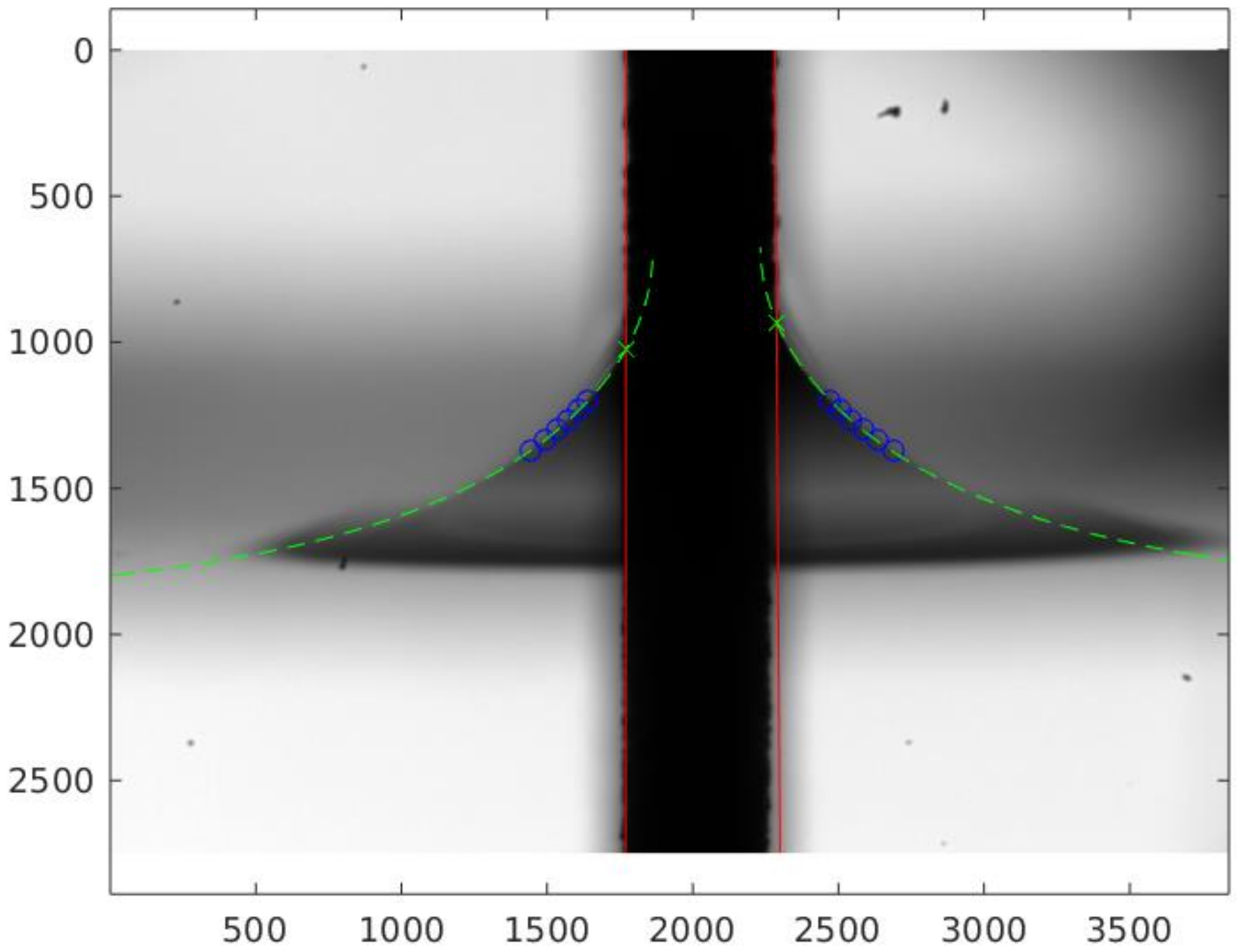
WP4 Characterisation

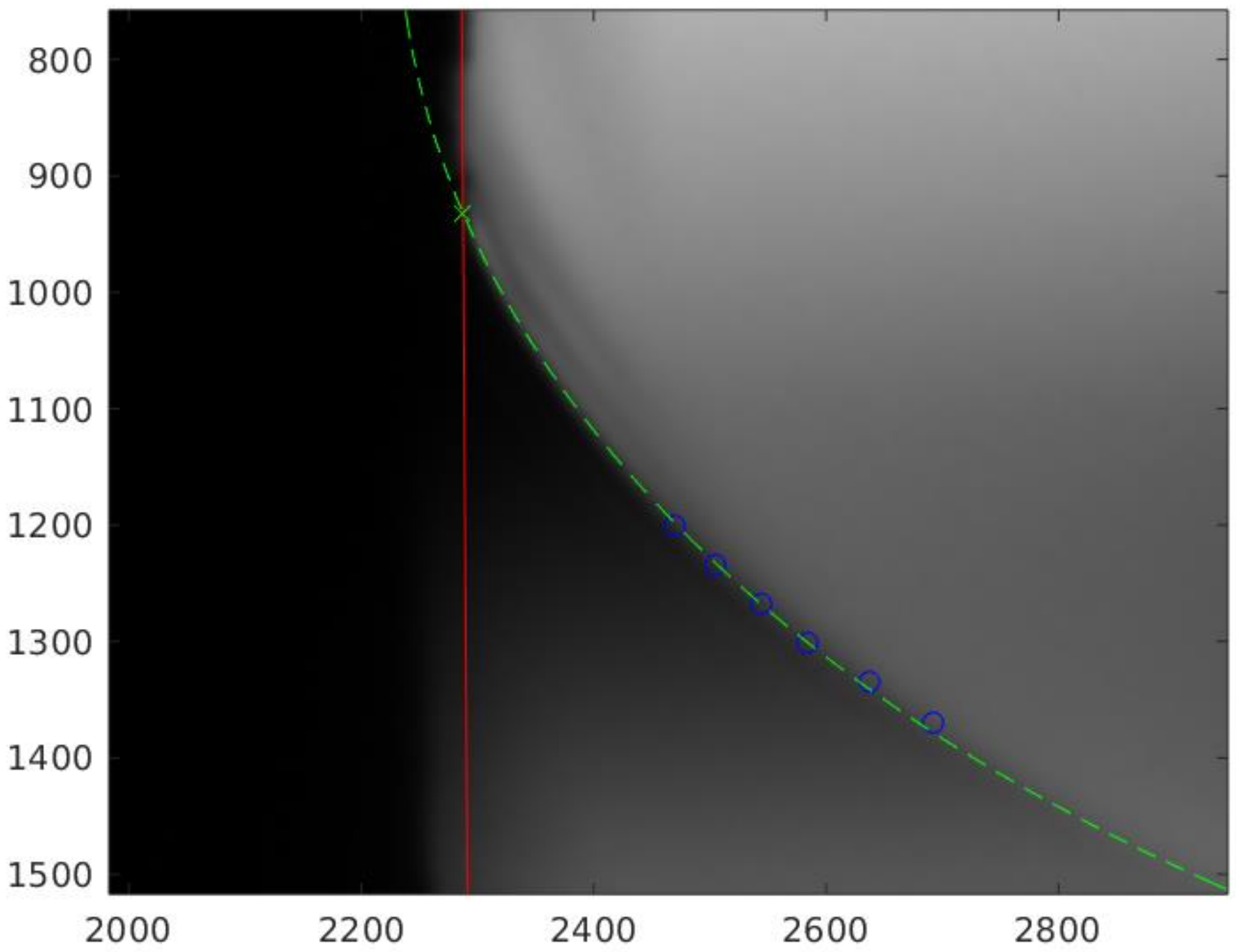
- **Wettability**
  - Meniscus at a single vertical wall



WP4 Characterisation

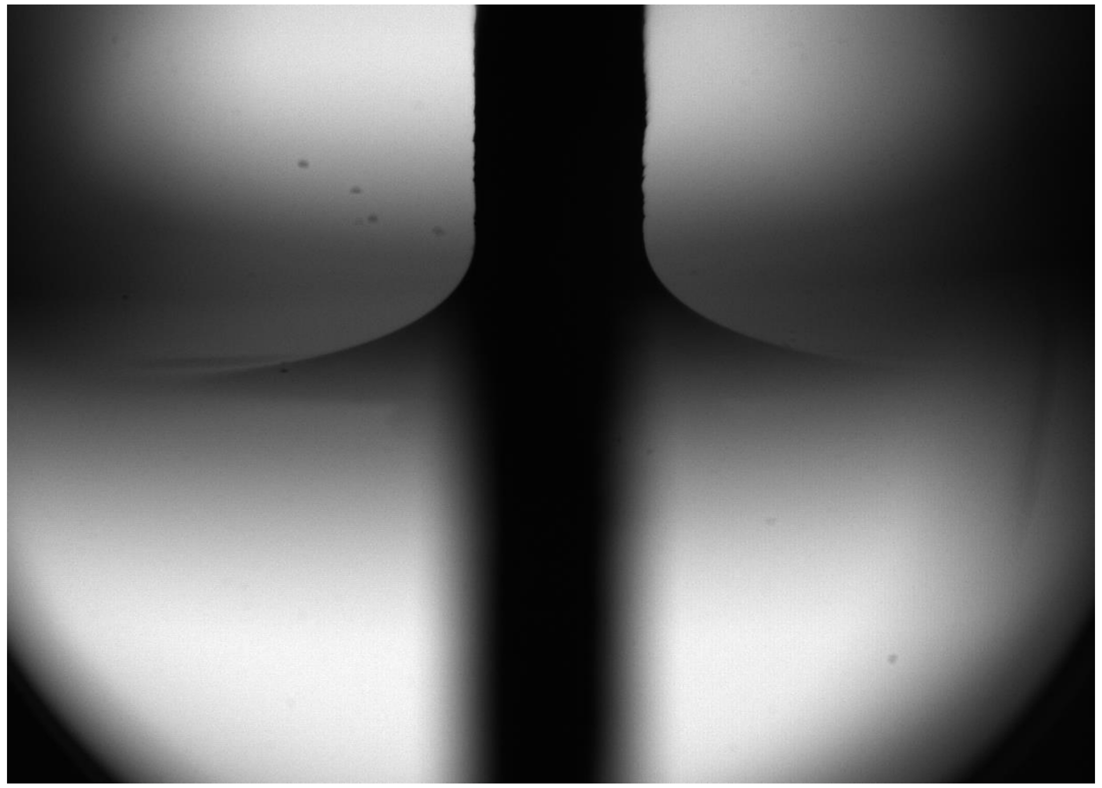
- **Wettability**
  - Meniscus at a single vertical wall



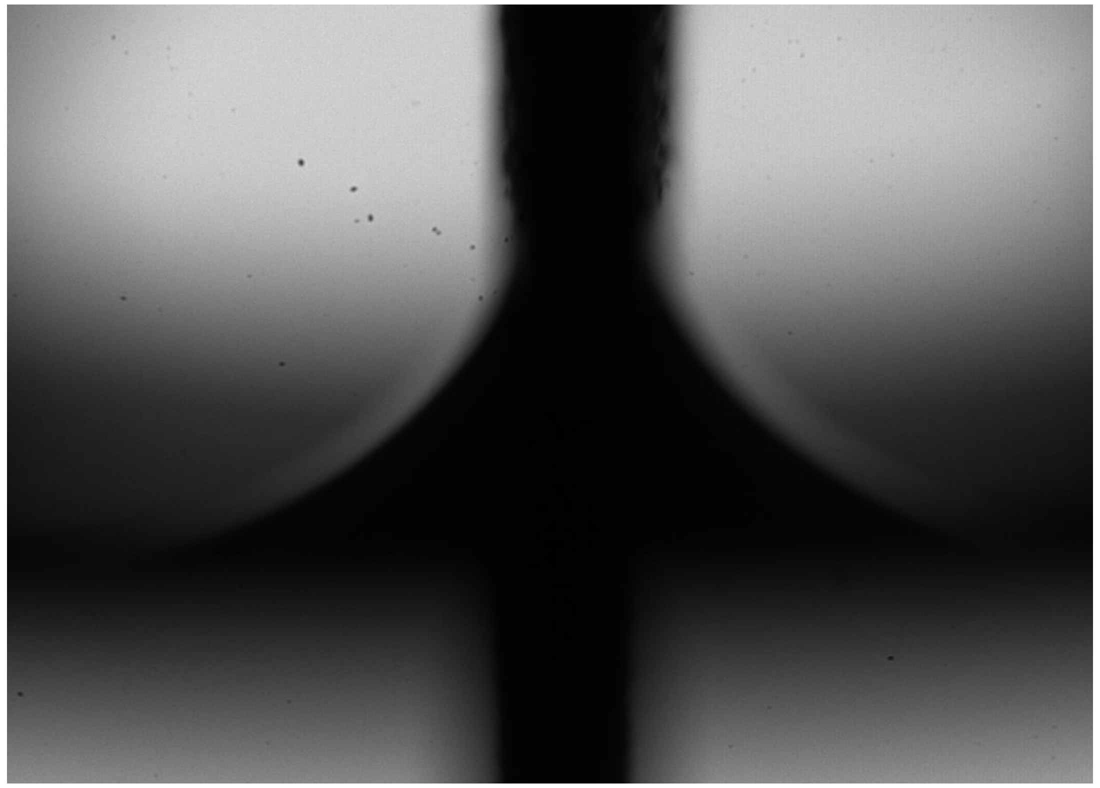


WP4 Characterisation

- **Wettability**
  - Approach works well for cylindrical samples where both sample and meniscus are in focus (DOF of lens of 1.2 mm.)
  - Doesn't work as well for rectangular samples as out of focus meniscus and wall close to camera block view of centre of sample



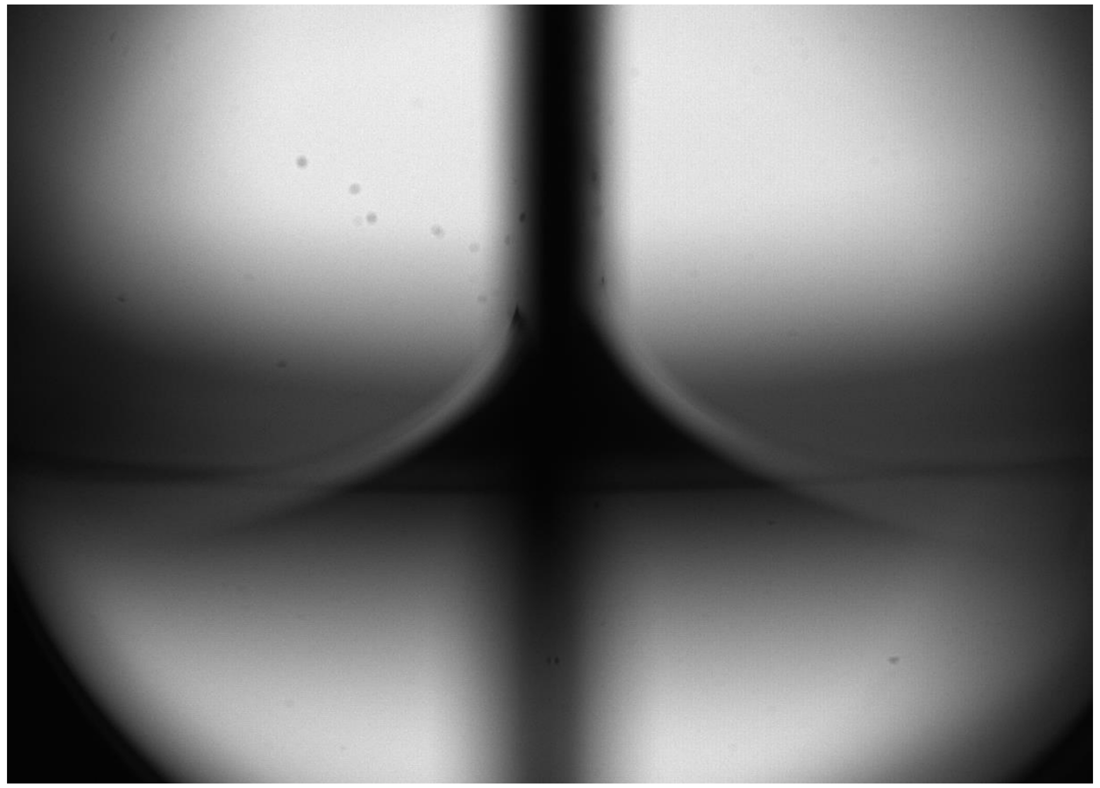
ALM Cylindrical sample



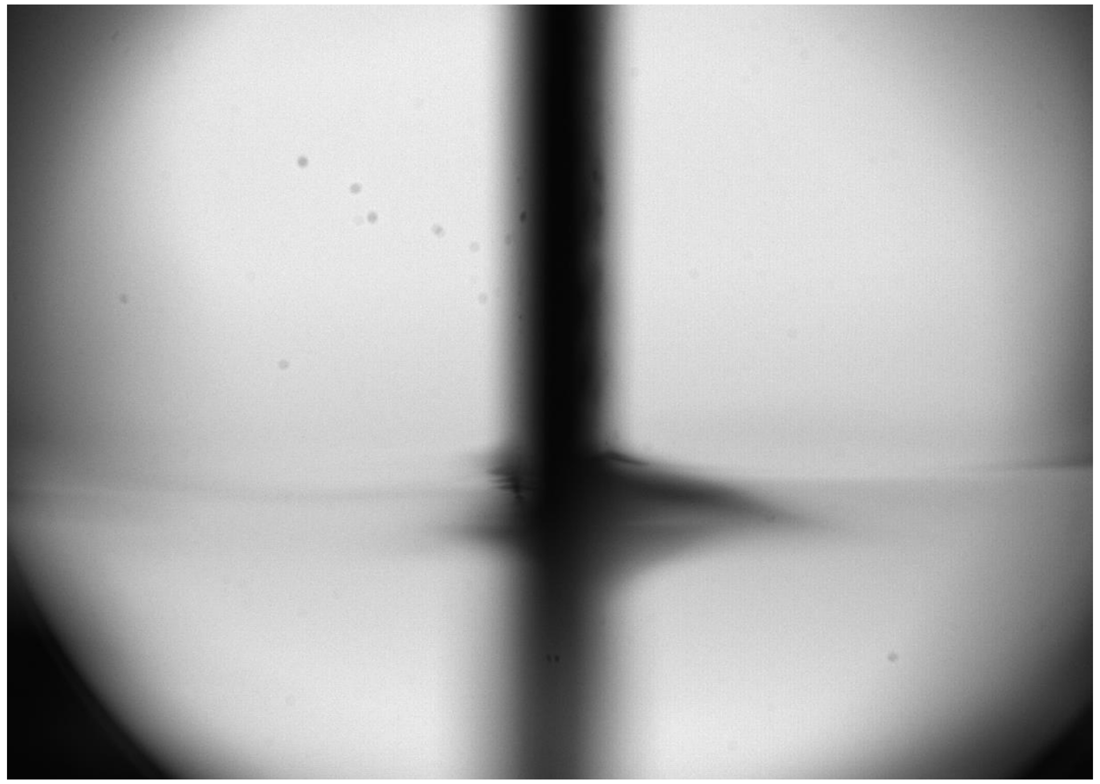
ALM Rectangular sample

WP4 Characterisation

- **Wettability**
  - Comparison sample of **Al6061** standard material with water:
  - Finely polished and surface roughness measured as Ra = 0.038 µm (AlSi10Mg ALM Ra = 12.48 µm)
  - Difficulty seeing receding CA (≈ or >90°) due to meniscus on viewport blocking view.
  - Results are close to values in literature (Advancing CA = 47°, Receding CA = 99°) [*Smith et al., 2014*]



Advancing CA



Receding CA

WP4 Characterisation

- **Wettability**
  - Imaging complete for Water, Methanol and Acetone.
  - Processing of images for CA measurement ongoing.
  - Results for Acetone:

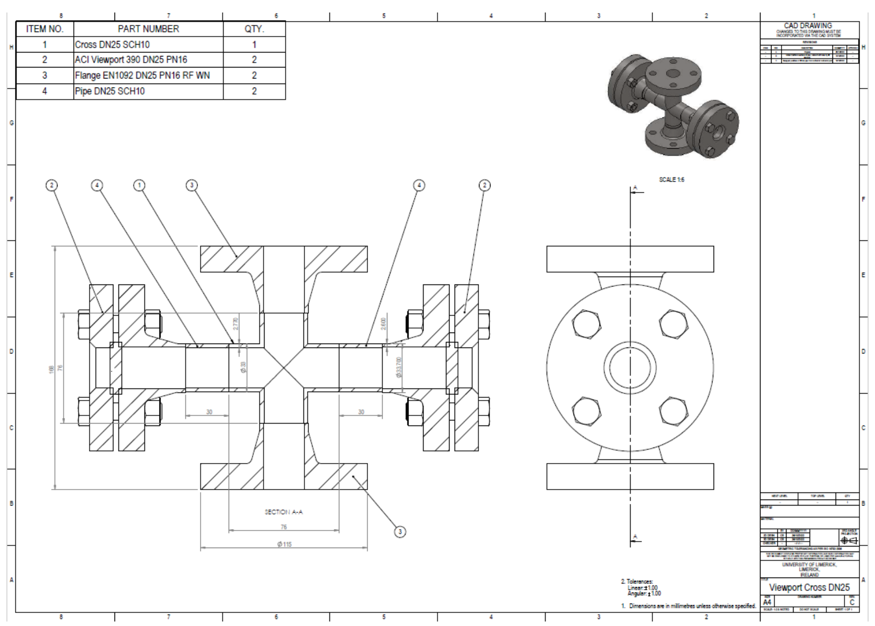
Metal	Advancing CA (°)	Receding CA (°)
Al6061	24.6	19.9
SS316L ALM	26.6	21.4
Ti6Al4V	23.7	20.4
AlSi7Mg	21.7	25.2
AlSi10Mg	30.4	27.3
Invar	28.5	27.7

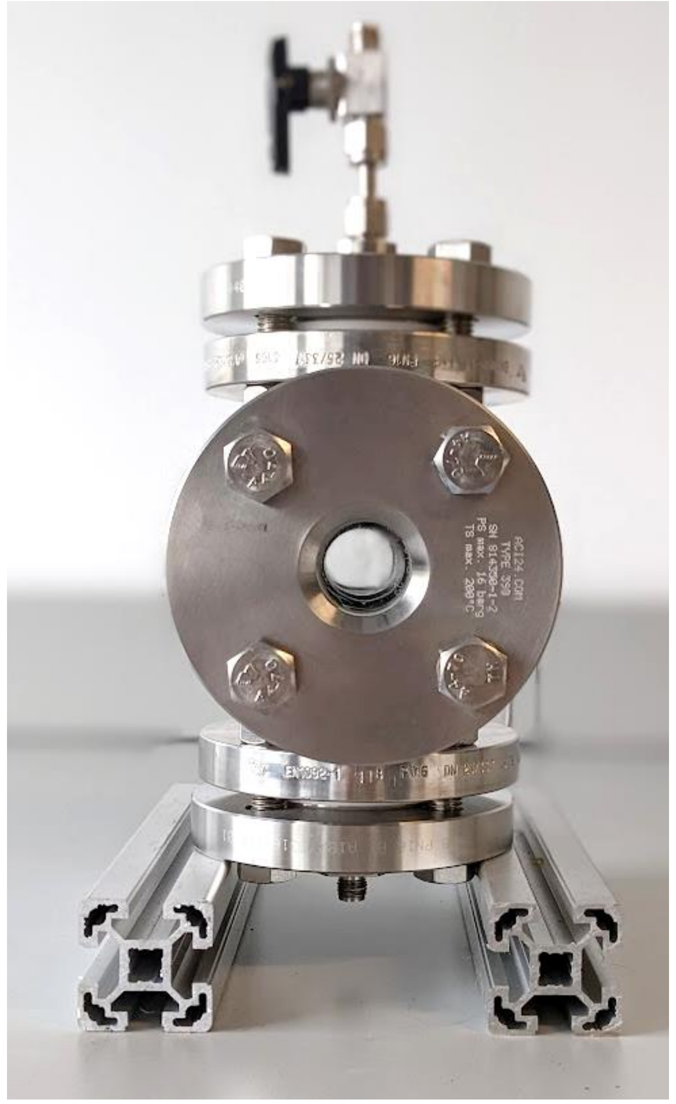
(average of left and right side for cylinder samples)

UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

WP4 Characterisation

- **Wettability**
  - High pressure setup: custom stainless steel DN25 PN16 four way cross with view ports.
  - Proof pressure test to 16 bar(g).



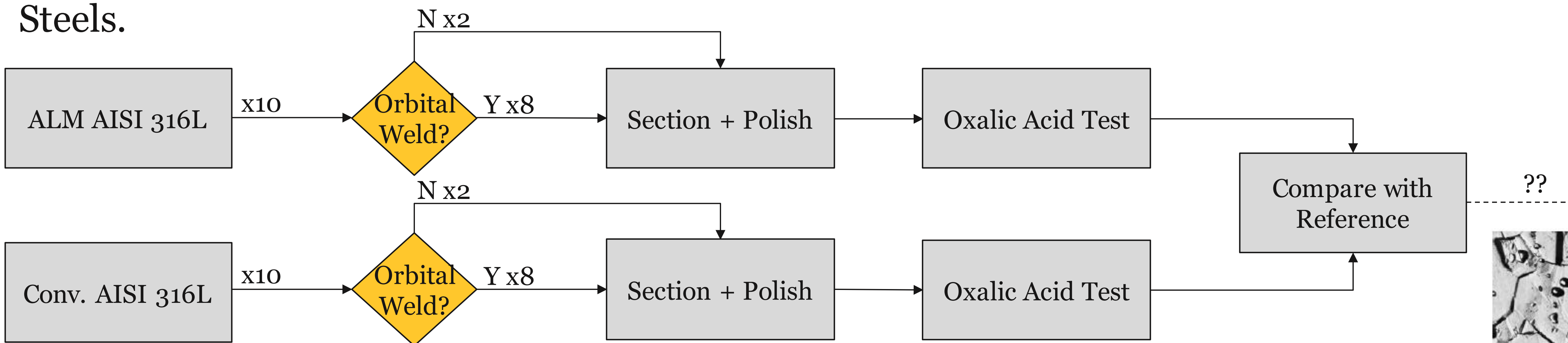


Anhydrous Ammonia cylinder (6kg)

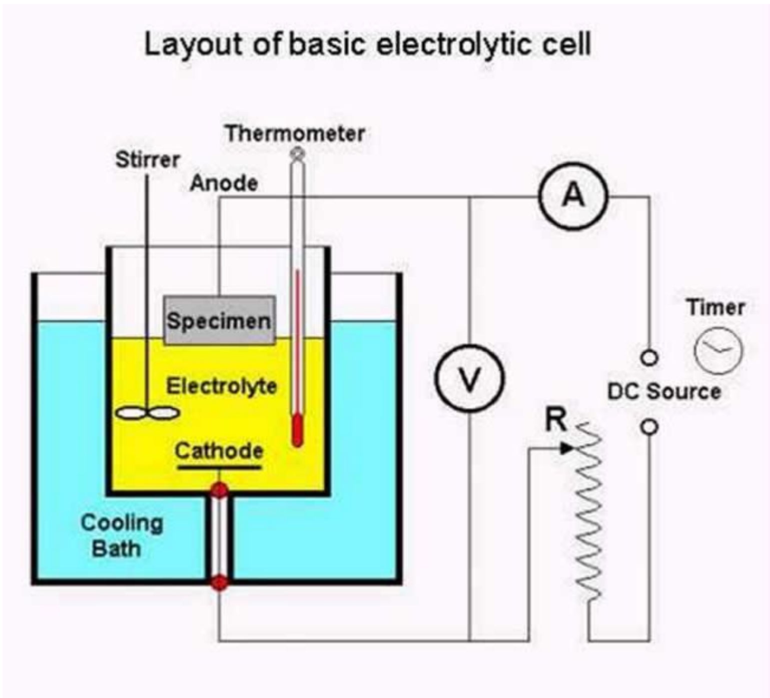
UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

WP4 Characterisation

- **Intergranular Corrosion Analysis of Orbitally Welded ALM SS 316L**
- **ASTM 262:** Standard Practices for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels.



Description	OD [mm]	Wall thickness [mm]	Length [mm]	Quantity
Main tube	12.7	0.9	25	20
Filling tube	6.35	0.9	40	10



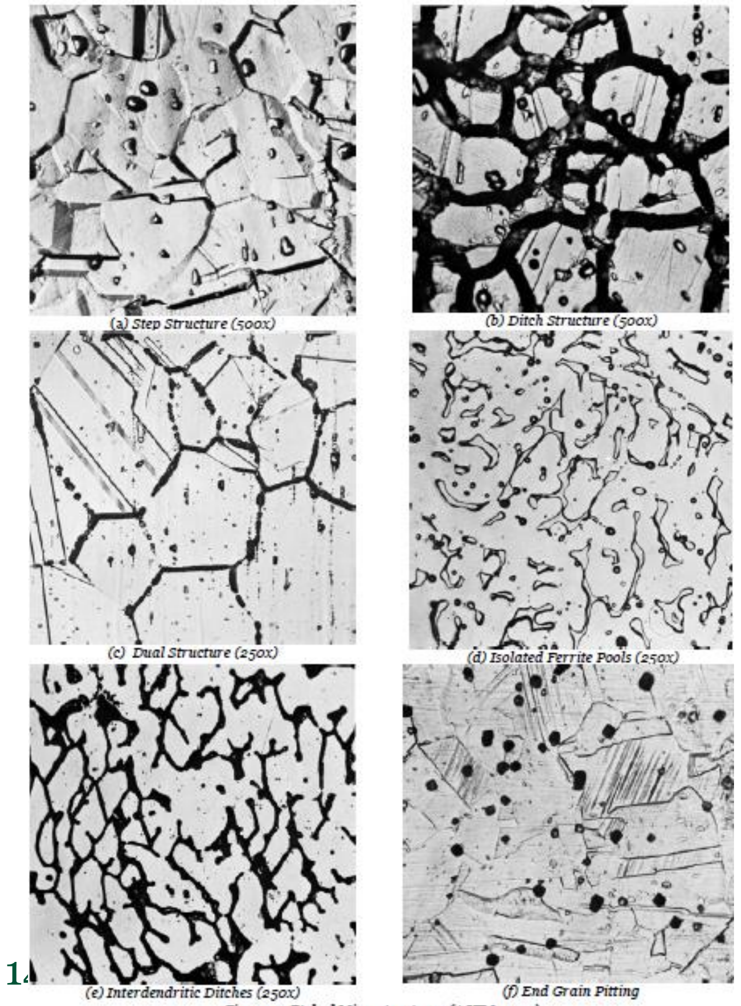


Figure 2: Etched Microstructures (ASTM, 2021)

WP4 Characterisation

- **Intergranular Corrosion Analysis of Orbitally Welded ALM SS 316L**
- **ASTM 262:** Standard Practices for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels.
- Orbital welding complete for 3 combinations:

Conv.-Conv. **Conv.-ALM** **ALM-ALM**

WP5 Conclusions and Recommendations

- Broad study investigating chemical compatibility for ALM metals with different working fluids.
- Generally good compatibility in most cases, other than a small number of exceptions.

	ALM					SCouP			Conventional		Bimetal.
	SS316L	Ti6Al4V	Invar	AlSi10Mg	AlSi7Mg	SS316L	AlSi10Mg	AlSi7Mg	SS316L	Al6061	
Acetone											
Ammonia											
E. Glycol											
Methanol											
Propylene											
Toluene											
Water											

- 2 water cases need further investigation.

University of Limerick – Ollscoil Luimnigh | Bernal Institute

WP5 Conclusions and Recommendations

- ALM **surface roughness** is main significant issue affecting all stages of manufacture and operation:
  - Welding
  - Sealing / connection to ports / couplings
  - Crimping
  - Cleaning
  - Loose particles
  - Wettability
- Improvements at printing stage needed to minimise surface roughness.
- Post-processing:
  - Machining of critical surfaces may still be necessary.
  - Treatments such as Electropolishing can provide > 50% reduction in roughness, but it is less effective on internal surfaces or complex geometries [*Chaghazardi & Wuthrich, 2022*].

WP5 Conclusions and Recommendations

- Specific **cleaning procedures** for ALM materials need to be developed.
  - Connected to surface roughness issue, as cleaning times will vary due to surface condition.
  - Alloys such AlSi7Mg and AlSi10Mg cannot be acid cleaned without severe attack.
  - Little public information on recommended cleaning practices.

- Specific **heat treatments** for ALM materials needed compared to conventional materials [*Haghdadi, et al., 2021*].
  - As-built material can be brittle, making crimping difficult.
  - Has been shown in literature to reduce surface roughness.
  - Improve isotropy of its microstructure and change mechanical and thermal properties.

UNIVERSITY OF LIMERICK OLLSCOIL LUIMNIGH | Bernal Institute

Thank you

contact: colin.butler@ul.ie

UNIVERSITY OF LIMERICK
OLLSCOIL LUIMNIGH
Bernal Institute

University of Limerick,
Limerick, V94 T9PX,
Ireland.

Ollscoil Luimnigh,
Luimneach,
V94 T9PX, Éire.

+353 (0) 61 202020

bernalinstitute.com