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**FRIEND
SHIP**

Forthcoming Research and Industry for
European and National Development of SHIP



Material selection and prototype design of a double-fluid circulation PCM storage for SHIP applications

SolarPACES 2021

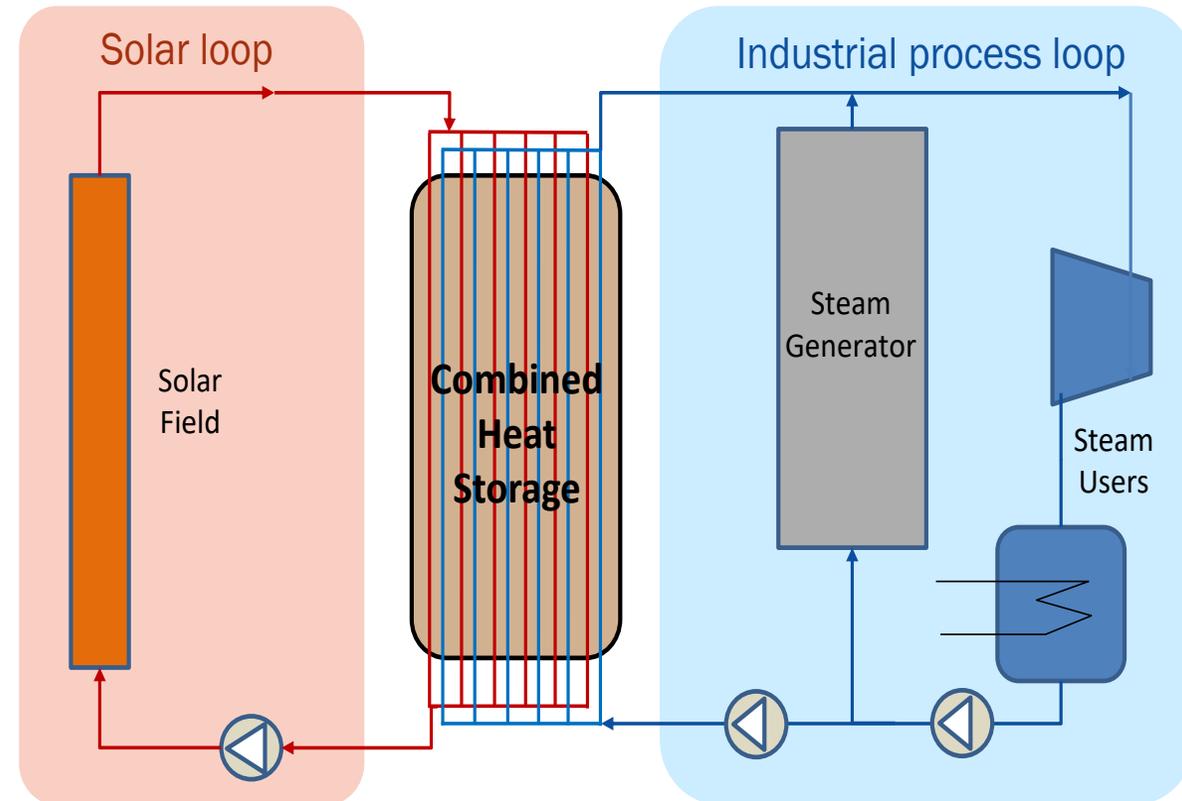
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Context

- ✓ Project objective
 - ✓ To demonstrate that SHIP is reliable, flexible, robust and cost-competitive
 - ✓ At temperatures between 200°C and 300°C
 - ✓ Industrial sectors such as textile, plastics, wood, metallurgy, and chemistry
- ✓ Thermal storage need
 - ✓ To ease the integration of SHIP in an existing process
 - ✓ A unique component with the following functions:
 - ✓ heat storage from solar field & from industrial process
 - ✓ heat release to the industrial process
 - ✓ direct heat transfer between solar and process loops using different HTFs
- ✓ Thermal storage solution:
Combined Heat Storage (CHS)



PCM review, selection and testing

Selected material

- Stability and performances OK
- **Thermo physical characteristics**
- Highly Hygroscopic
- High density

Type	Name	$\Delta H_{\text{sol/liq}}$ (J/g)	T_f (°C)	Comments	
Eutectic Mixture	$\text{Ca}(\text{NO}_3)_2\text{—KNO}_3$	70	152	Affordable, highly hygroscopic	Tested
Eutectic Mixture	$\text{NaNO}_3\text{-Ca}(\text{NO}_3)_2\text{—KNO}_3$	Very low	180	Affordable, highly hygroscopic	Tested
Sugar and sugar alcohol	d-Mannitol	294-341	165-168	High supercooling and stability issues	Tested
Eutectic mixture	$\text{LiNO}_3\text{-NaNO}_2$	233	156	High Cost, highly hygroscopic	
Eutectic mixture	$\text{LiNO}_3\text{-KCl}$	272	160	High Cost, highly hygroscopic, corrosion issues	
Eutectic mixture	HCOONa-HCOOK	175	176	Scarce existing data, corrosion issues	
Inorganic salt	Potassium thiocyanate	112-114	157-177	Low cycling stability, corrosion issues, toxicity	
Fatty acid	Adipic acid	239-252	152	Flammable at temperatures $>170^\circ\text{C}$, corrosion issues	Tested
Amide	Benzanilide	129-139	161	Produce CMR and flammable gas upon decomposition	
Phenolic acid	Salicylic acid	199	157-159	Low cycling stability, highly flammable	
Aromatic hydrocarbon	Hydroquinone	179-235	160-173	Low cycling stability, highly flammable, CMR?	
Sugar and sugar alcohol	Dulcitol	246-257	167-185	Low cycling stability, supercooling	

Material characterization - binary mixture

Proportions mixed and heated 4h @ 250°C, then characterized

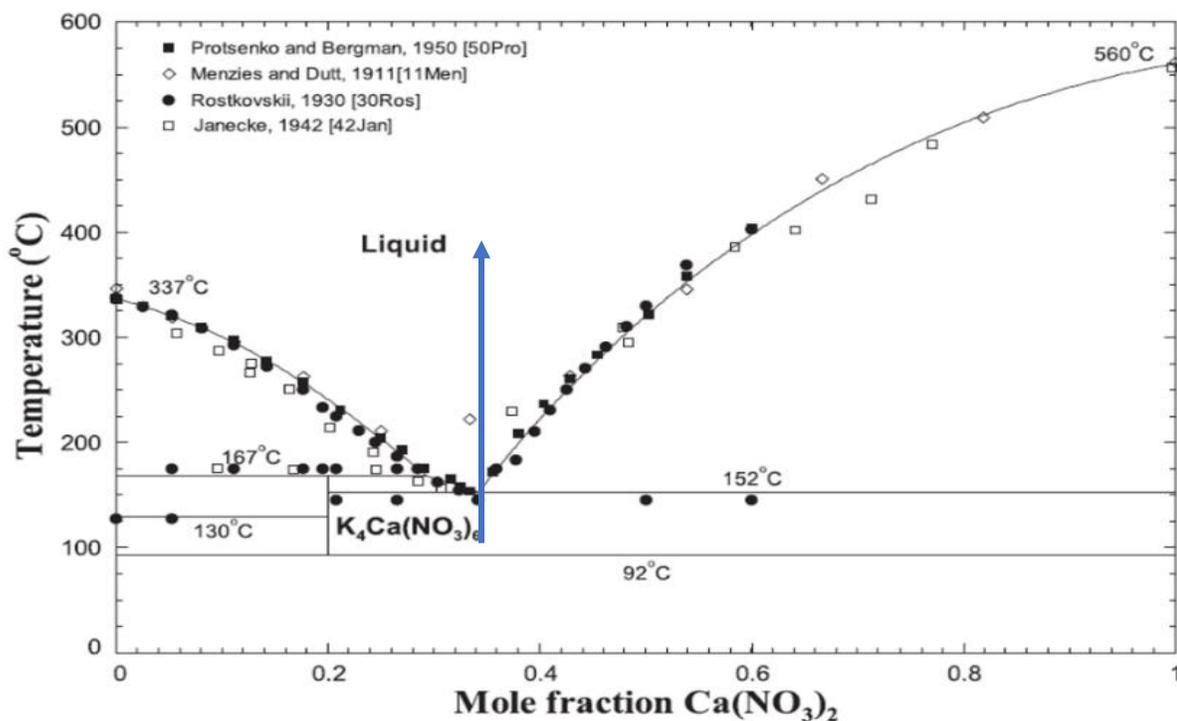
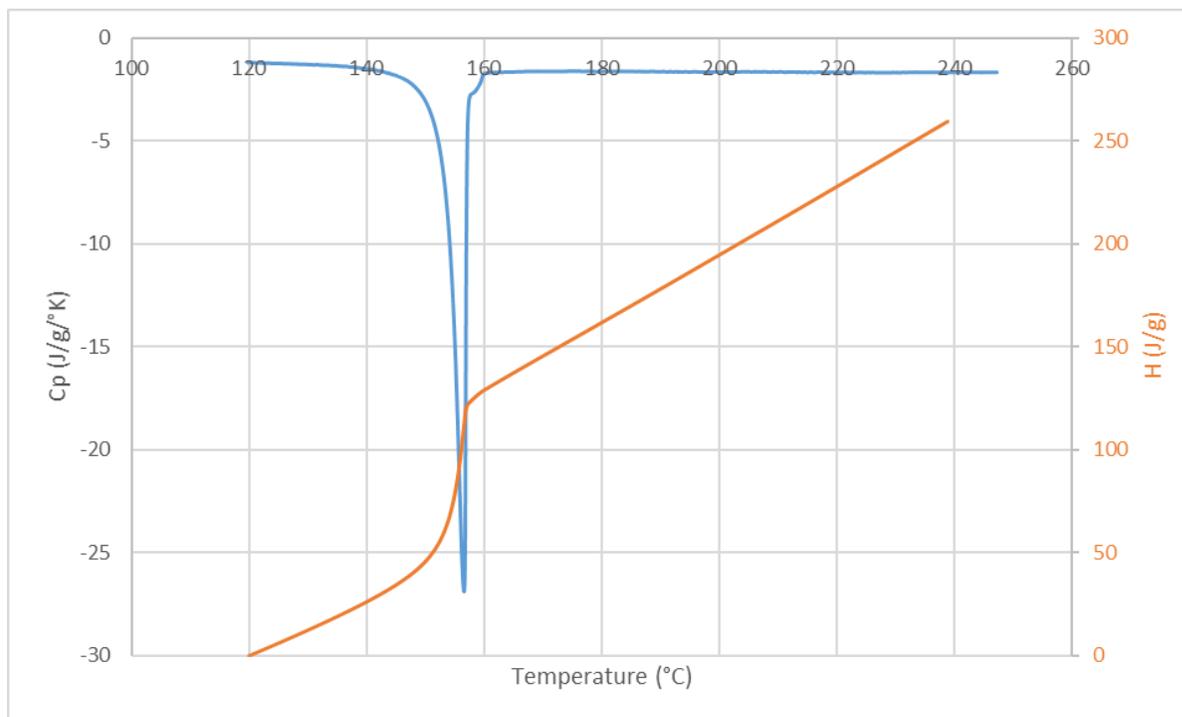


Figure 1. Calculated $\text{KNO}_3\text{-Ca(NO}_3)_2$ phase diagram.

Source: Chartan et al., 2019, The Journal of Chemical Thermodynamics, 2019



$T_{\text{onset}} = 152^\circ\text{C}$, $H_f = 70 \text{ J/g}$, $H_{[140-180]} = 130 \text{ J/g}$
Density Solid @ 22°C : $2\,151 \text{ kg/m}^3$
Liquid @ 185°C : $2\,074 \text{ kg/m}^3$

Material characterization - effect of humidity

$\text{Ca}(\text{NO}_3)_2$ not available as anhydrous salt

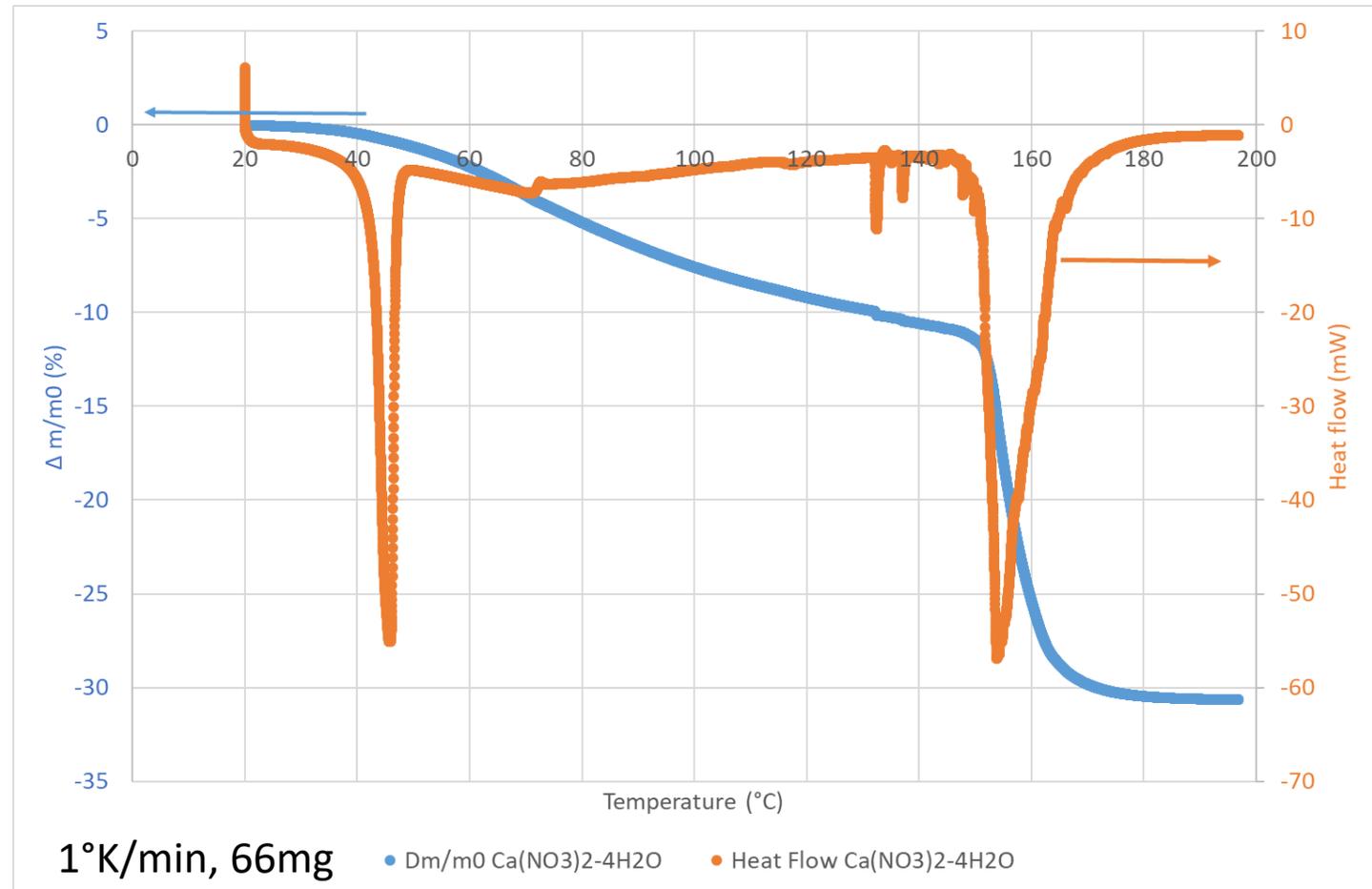
↳ Only $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in standard conditions

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$:

- Start dehydration below 40°C
- Fully dehydrated above 160°C
- Total mass loss: 30%wt

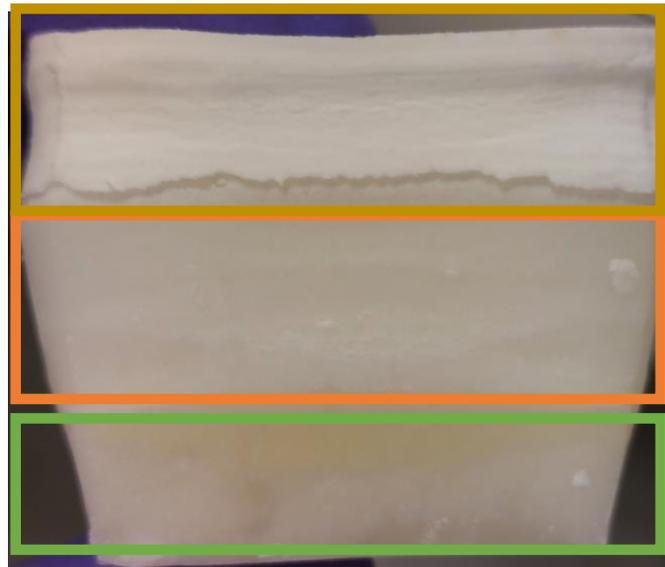


Effect of humidity on
binary mixture and impact
on the storage unit?

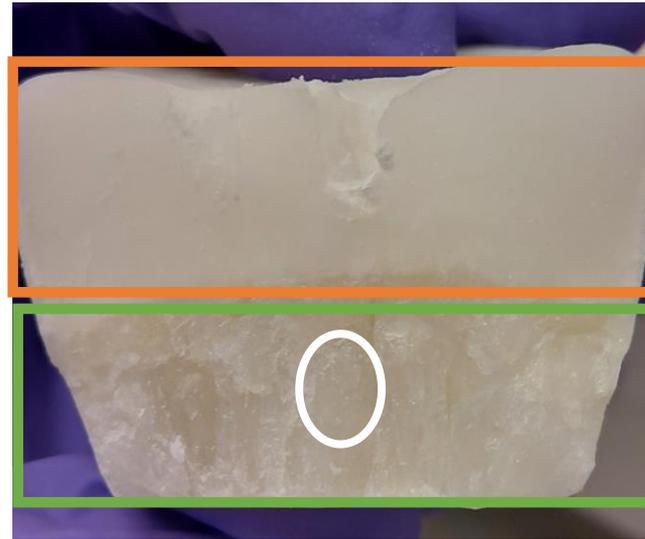


Influence of humidity on the binary material

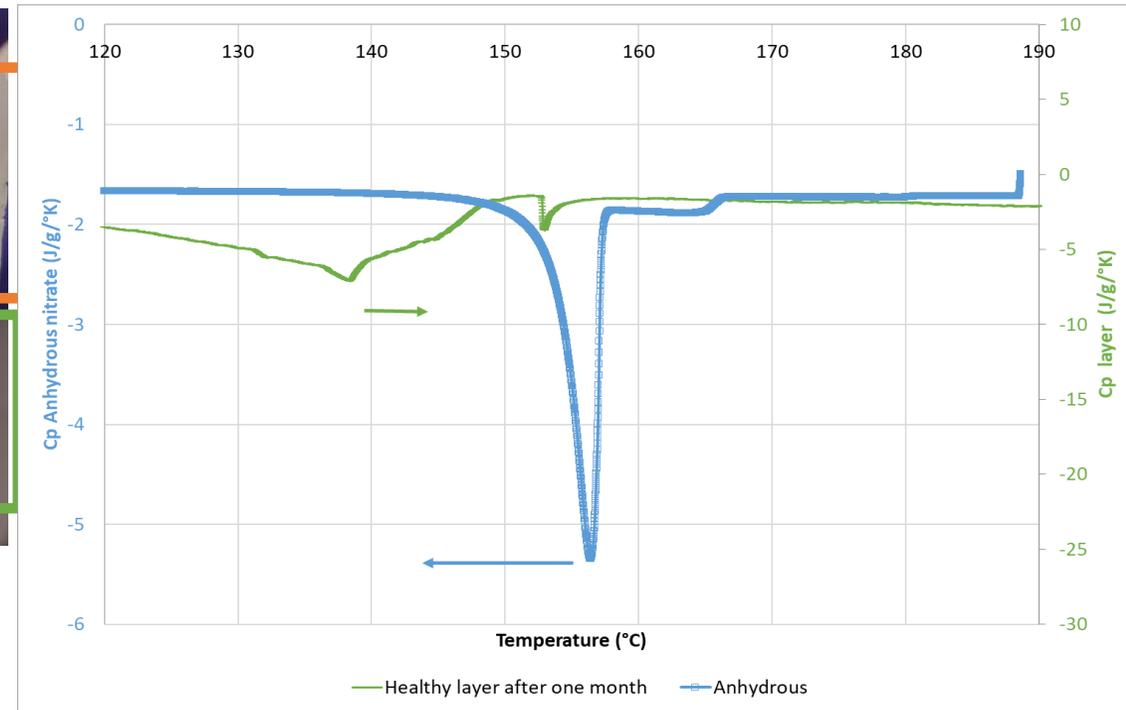
- 50g bulk anhydrous binary mixture left 3 weeks at 17°C/47%HR in an open container



External view



Cross section

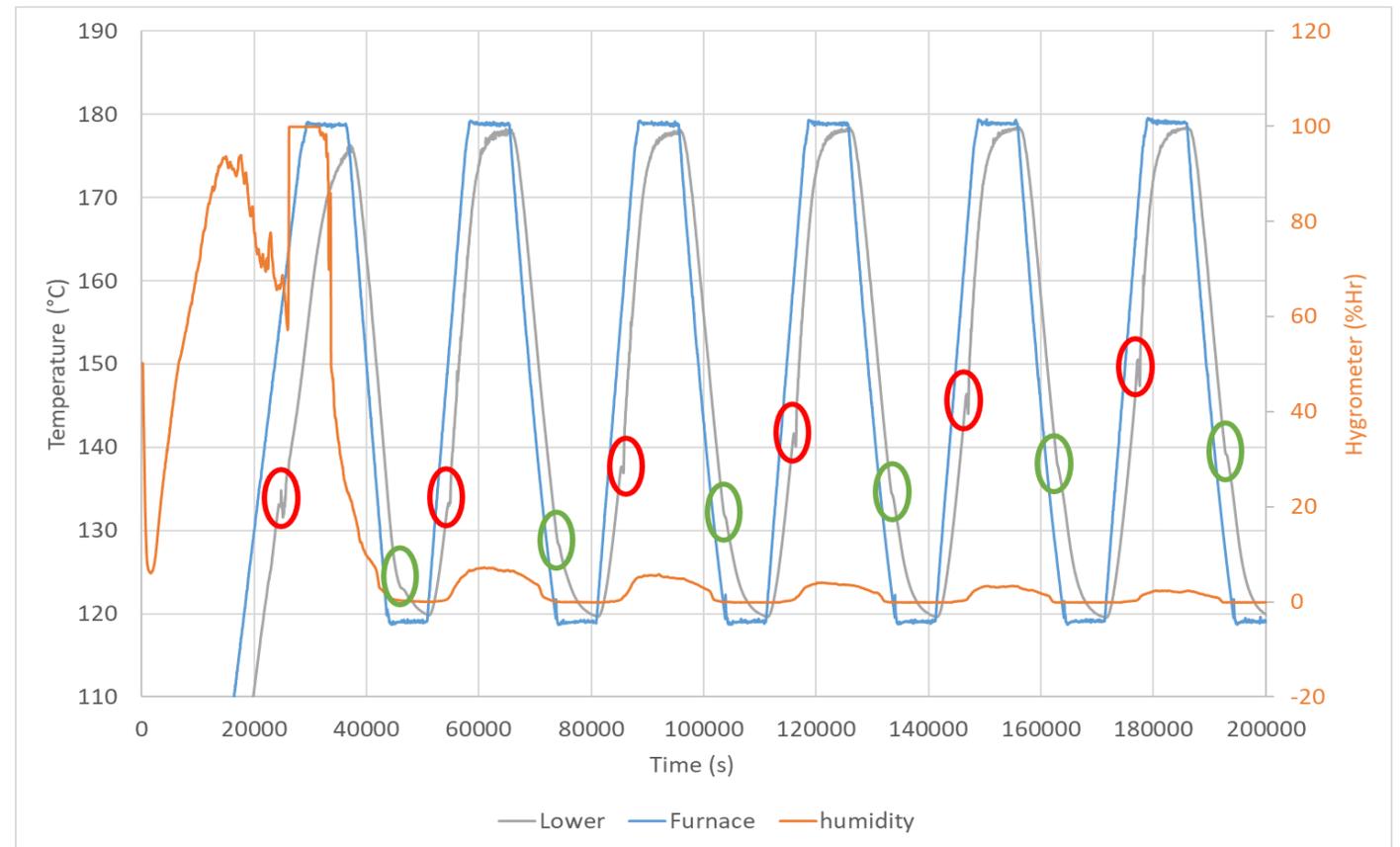
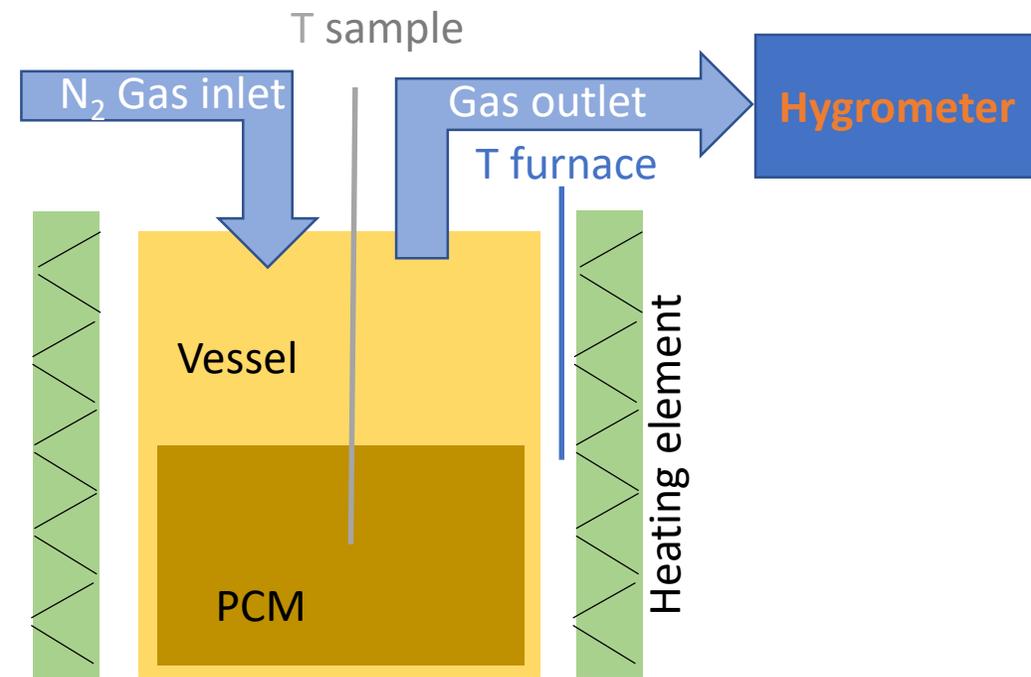


Water molecules modify the binary nitrate and make it unusable for heat storage

Is it possible to regenerate it?

Influence of humidity on the binary material

Anhydrous binary salt, grinded left 3 weeks
at 17°C/47%Hr



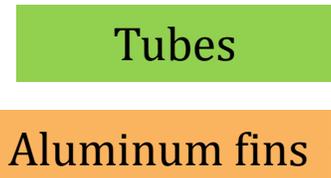
Melting/solidification temperature increases as humidity drops → binary nitrate « regenerates »

PCM storage design: state of the art

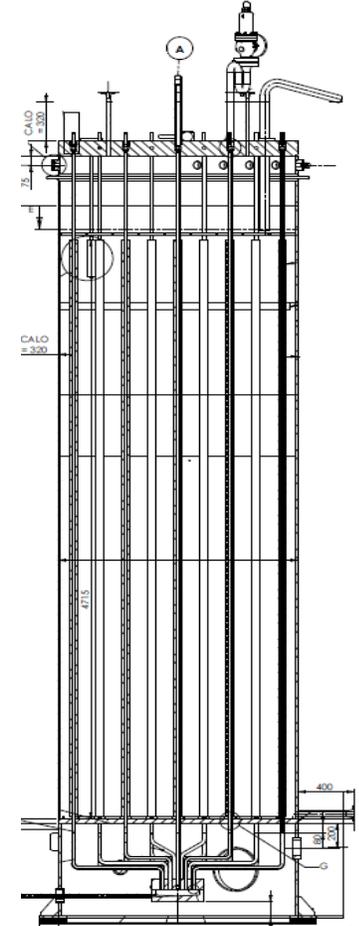
- ✓ PCM storage prototypes for CSP application
 - ✓ Shell and tube design
 - ✓ A unique HTF



PCM tubes & inserts



Heat transfer enhancement by aluminum inserts around the vertical finned tubes



PCM storage test section

Source: Garcia et al., 2020 SolarPACES Conference

Prototype integration & Design parameters

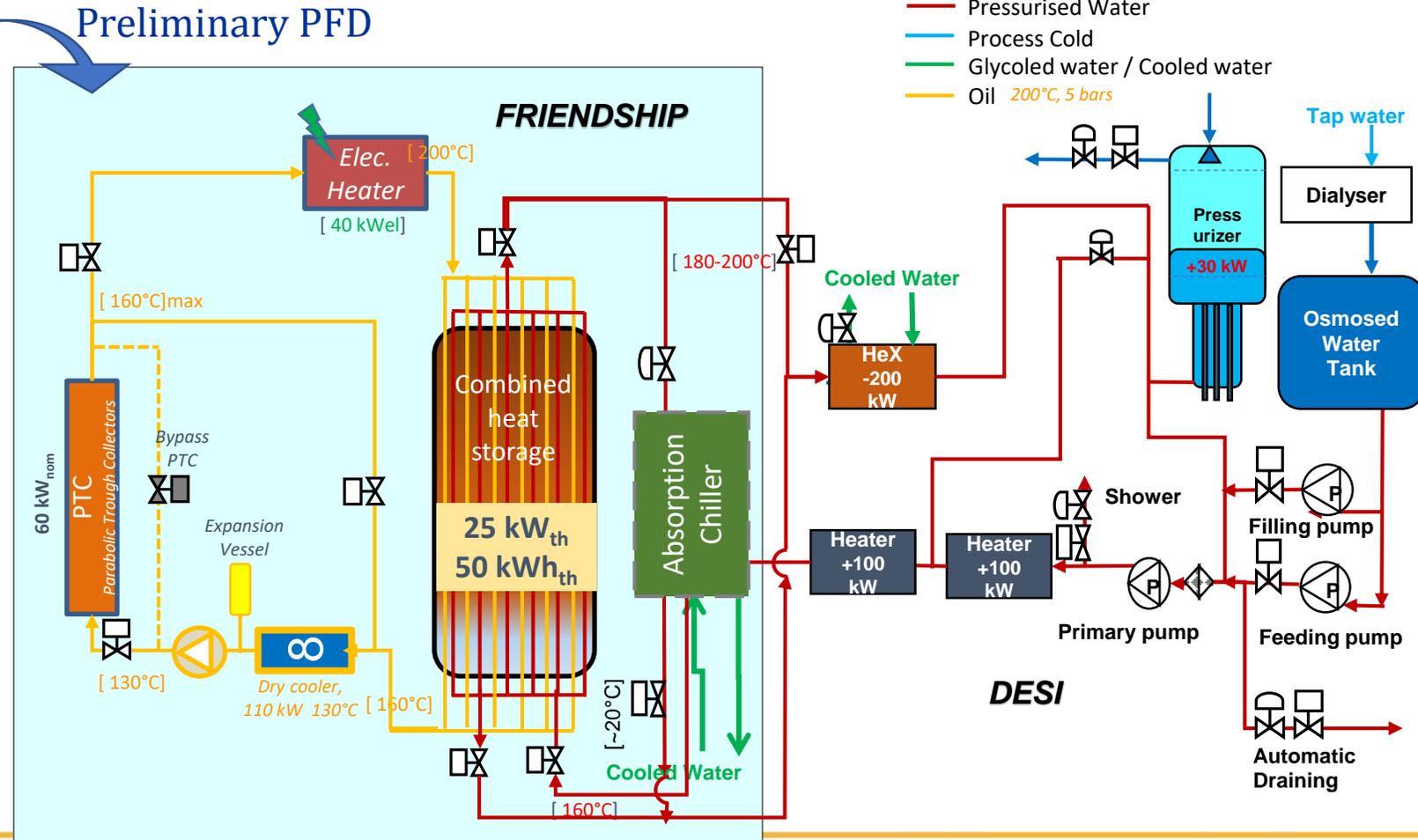
✓ Prototype tested on two facilities

HTF type	CHS Lab tests	SHIP200 prototype
From FRIENDSHIP heat producers	Pressurized water	Thermal oil
From / To existing process heat consumers	Steam	Pressurized water

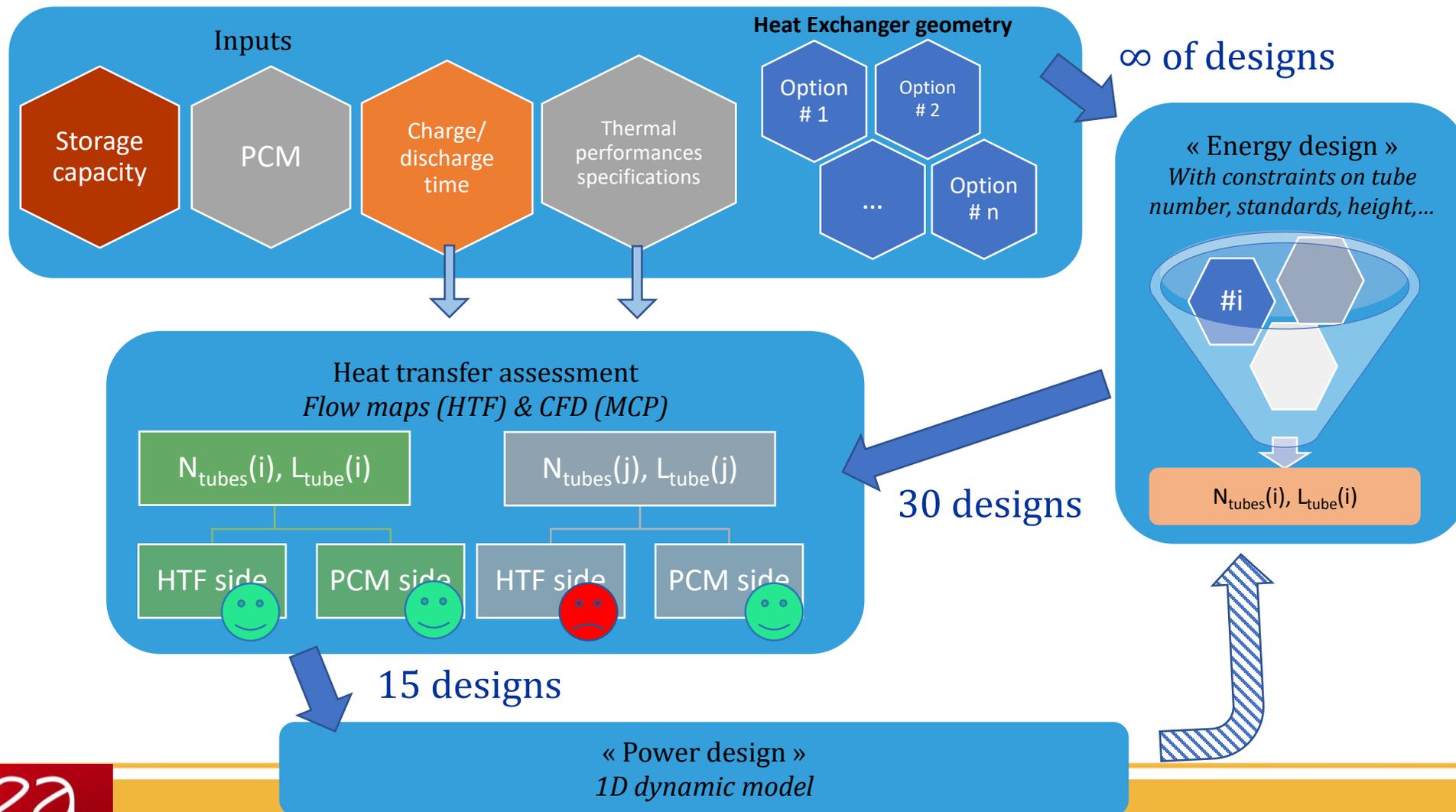
✓ Design conditions

	Charge	Discharge
Heat Transfer Fluid	Wacker Helisol XLP	pressurized water
Charging/discharging time	4 h	2 h
Inlet temperature	200°C	140°C
Pressure level - Nominal	5 bara	20 bara
Mean HTF temperature	178.2°C	148.2°C
HTF mass flow	156 g/s	354 g/s

Preliminary PFD

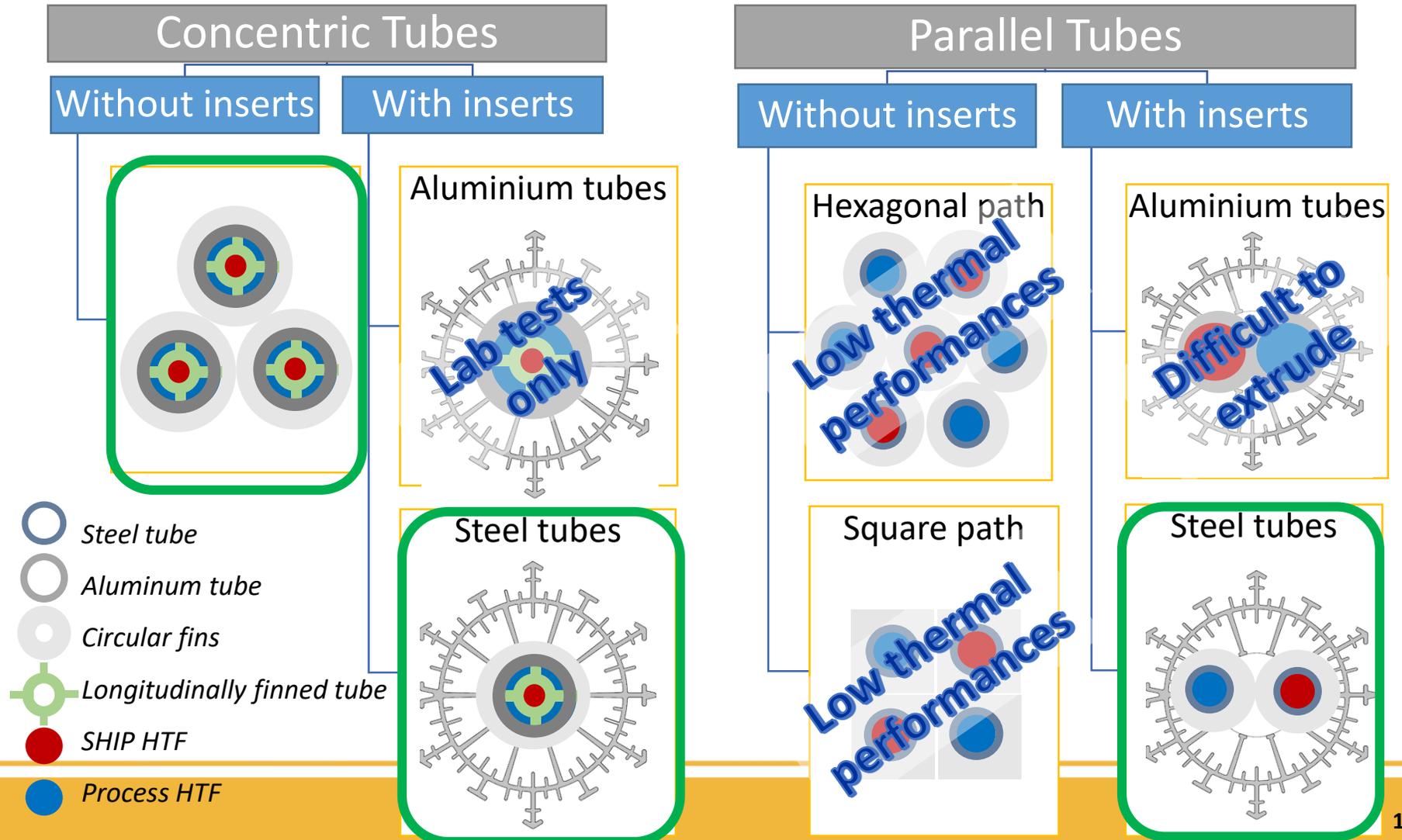


Design selection methodology



Possible two-fluid designs

- ✓ A wide range of possible designs
 - ✓ Aluminium heat exchanger tubes: would need enhanced thermomechanical resistance and corrosion tests
 - ✓ Extrusion limits for aluminium inserts
 - ✓ Standard finned tubes only



Sizing results

Design	Option A	Option B	Option C
D_{in}/D_{out} charge tube (mm)	13.65 / 19.05	13.65 / 19.05	10.48 / 15.88
D_{in}/D_{out} discharge tube (mm)	32.7 / 38.1	32.7 / 38.1	10.48 / 15.88
D_{out} fins (mm)	63.5	63.5	34.88
Tube spacing (mm)	96	70	88
Number of double fluid tube	29	61	37
Tube length (m)	3.64	3.52	3.87
[CFD] ΔT_{max} end of discharge (K)	4.0	2.6	9.3
[1D model] Charged energy*	85% ▲	95% ▲	82% ▲
[1D model] Discharged energy*	98% ○	107% ○	87% ○

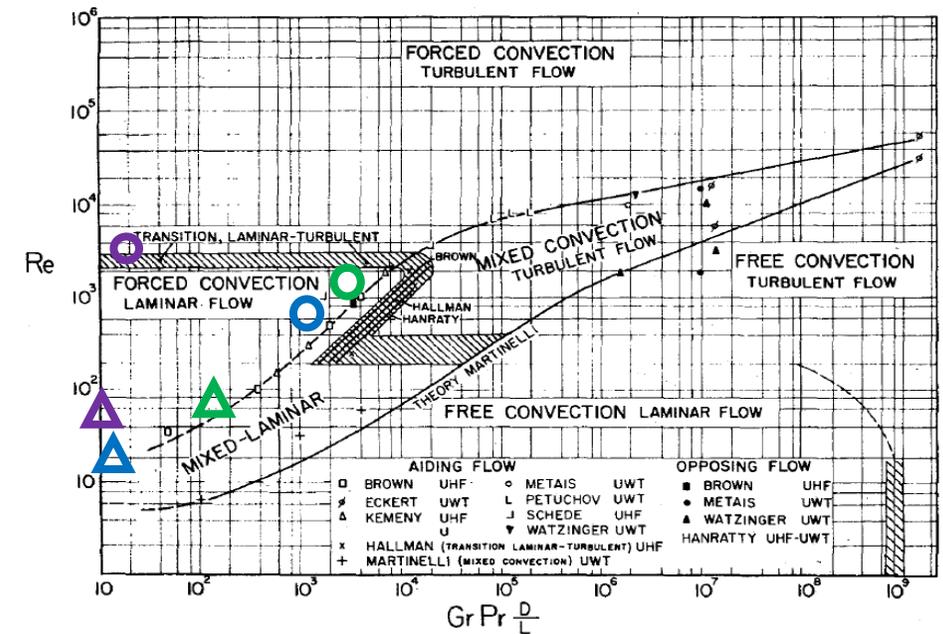


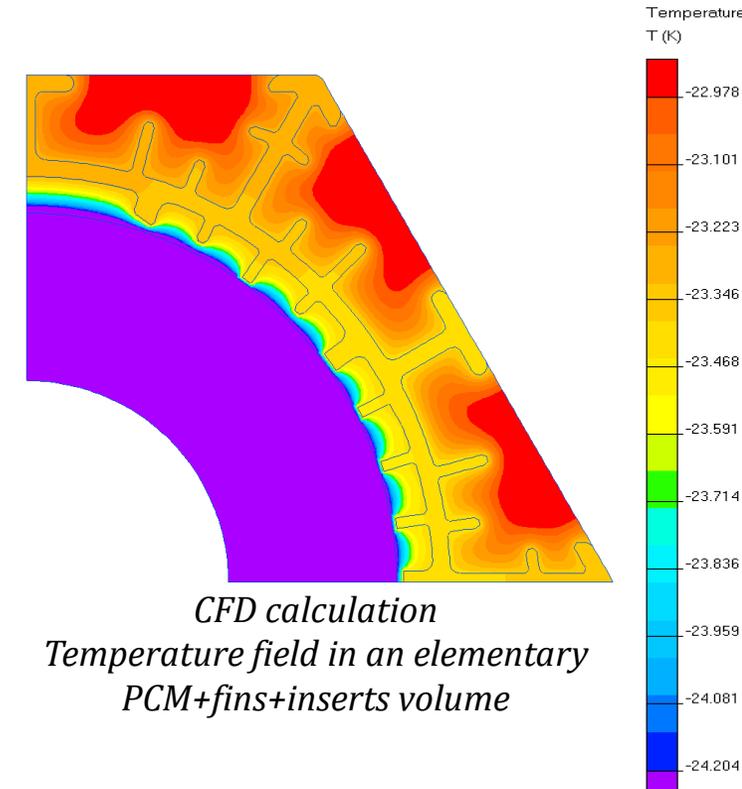
Fig. 1 Regimes of free, forced, and mixed convection for flow through vertical tubes

$$(10^{-2} < Pr \frac{d}{L} < 1)$$

Source: Metais & Eckert *Journal of Heat Transfer* **86** 295-6 1964

Conclusions & Outlook

- ✓ Low cost and non corrosive PCM selected and characterized
 - ✓ Not a lot of choice in this temperature range! Very few data in literature
 - ✓ Ongoing work on humidity management and filling procedures
- ✓ A wide range of prototype designs considered
 - ✓ CFD and 1D system model to assess thermal performances
 - ✓ Ongoing engineering study with promising designs for the 3 options
 - ✓ With cost estimates from potential manufacturers
- ✓ Perspectives
 - ✓ CHS storage adapted to numerous storage applications: district heating, Carnot batteries, waste heat recovery,...
 - ✓ Concentric designs show high heat transfer rates and can be used as heat exchangers



Thanks for your attention!



FRIENDSHIP WP5 team: Pierre Garcia, Gilles « Walter » Matringe, Grégory Largiller, Célian Jean

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