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Adjustable Cryo PCM Blankets

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Executive Summary Report

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1 Abbreviations

Abbreviation	Synonyms
AAO	Anodic Aluminum Oxide
ACPB	Adjustable Cryo PCM Blanket
AD	Applicable Document
AG	ArianeGroup GmbH Bremen
AIT	Assembly, Integration and Test
BB	Breadboard
CMOS	Complementary Metal Oxide Semiconductors
DSC	Differential Scanning Calorimetry
ECSS	European Committee for Space Standardization
ESA	European Space Agency
ESR	Executive Summary Report
ESTEC	European Space Research and Technology Centre
FEM	Finite Element Method
ETI	External Thermal Insulation
FR	Final Report
HTS	High Temperature Super Conductor
I/F	Interface
IFAM	Fraunhofer Institute for Manufacturing Technology and Advanced Materials
LSI	Large System Integrator
MAIT	Manufacturing, Assembly, Integration & Test
MD	Molecular Dynamic
N/A	Not Applicable
OWS	Offshore Wind Solutions
PCM	Phase Change Material
QA	Quality Assurance
RD	Reference Document
RST	RST Rostock System-Technik GmbH
SEM	Scanning Electron Microscopy
TN	Technical Note
TSU	Thermal Energy Storage Unit
V&V	Validation & Verification
WP	Work Package
XPS	X-Ray Photoelectron Spectroscopy

2 Introduction

2.1 Scope of the Document

The present document describes the work performed within the de-risking activity Adjustable Cryo PCM Blankets providing a brief overview of the major findings, conclusions and further study areas.

2.2 Purpose of the de-risking activity

In the frame of *GSTP – Assessment to prepare and de-risk technology developments* program by the European Space Agency the first steps for the development of space qualified Adjustable Cryo PCM Blankets up to a test campaign of a technology demonstrator at laboratory scale have been taken.

These Adjustable Cryo PCM Blankets are intended to offer a new design solution for passive thermal control systems, which could be used on spacecrafts.
Key features of the ACPB could be summarized as follows:

- Thermal energy storage with phase change materials in the temperature range between 90 and 159 K. Solid / liquid phase change is used.
- For this investigation ethanol is used as PCM.
- Phase change temperature is intended be adjustable down to 90K by freezing point depression based on confinement of the ethanol in pores at the nanoscale (Gibbs-Thomson-effect).
- The problem of the low thermal conductivity of ethanol is inherently solved by the surrounding high conductive material, i.e. the perforated aluminum foil as nanoporous matrix and the sealing aluminum foil.
- The blankets are flexible and to increase the performance several foils can be super-imposed thermally coupled with each other.

3 Findings

3.1 Identification of Launcher and other Space Applications

Covered Work packages: WP2100, WP2200, WP4200

3.1.1 Identification of Space Applications

Applied to a spacecraft two key performance characteristics could be addressed to the ACPB:

- Cryo PCMs either smooth temperature variations of a component under periodically changing ambient conditions / thermal dissipations.
- Or Cryo PCMs are utilized to continue the cool chain of a component during limited periods of occasional higher heat flux, during which the peak heat flux is damped in the PCM.

Ten applications for Adjustable Cryo PCM Blankets (ACPB) on spacecrafts have been described:
Launcher applications:

1) Increase of Solar Cell Efficiency for Future Under-Fairing Upper Stages
2) Increase of Cold Gas Thruster Specific Impulse for Future Upper Stages
3) Continuous Cooling of HTS for Future Upper Stage's Propellant
4) Zero Heat Flux into Propellants during Launcher's Ascent Phase
5) Effective Cooling for Future Upper Stage's Cryogenic CMOS Technology

Satellite applications:

6) Increase of Solar Cell Efficiency for Low Earth Orbit Satellites
7) Effective Cryo Management of Detectors
8) Effective Cooling of Cryogenic Low Noise Amplifiers for Future Satellites

Extraterrestrial applications:

9) Increase of Solar Cell Efficiency of Mars Rovers
10) Continuous Cooling of Samples

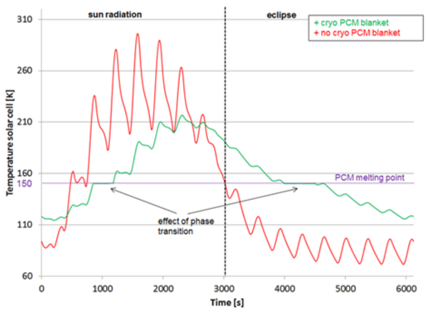
3.1.2 Thermal Performance Assessments

The following two applications have been selected for further processing within this study in the form of thermal performance assessment with ESATAN TMS:

- Increase of Solar Cell Efficiency for Future Under-Fairing Upper Stages.
- Increase of Cold Gas Thruster Specific Impulse for Future Upper Stages.

3.1.2.1 <u>Thermal Performance Assessment – Increase of Solar Cell Efficiency for Future Under-Fairing Upper Stages</u>

The results of the thermal analysis are shown in Figure 3-1.



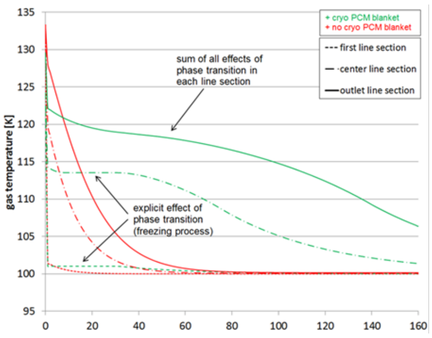
Indicator	With ACPB (T_{melt} = 150K, $\Delta T_{depress}$ = 9K)	Without ACPB (reference)
Average electrical power [W/m²]	45.3	40.9
Gain in electrical power [%]	+ 10.8	
Additional mass [kg/m²]	+ 2.6	

Figure 3-1: Thermal Performance Assessment - Increase of Solar Cell Efficiency

In conclusion, for the configuration studied here, the solar cell with ACPB attached to the backside yields about 11% more electrical power in average compared with the reference case without ACPB.
This gain is at the cost of an additional mass of only 2.6kg/m² by the ACPB.

3.1.2.2 Thermal Performance Assessments - Increase of Cold Gas Thruster Specific Impulse

The results of the thermal analysis are shown in Figure 3-2.



Indicator	With ACPB (T_{melt} = 122K, $\Delta T_{depress}$ = 37K)	Without ACPB (reference)
$\langle SQRT(T_t) \rangle_{t_{on}}$ [√K]	10.75	10.17
Gain in specific impulse [%]	+ 5.7	
Additional mass [kg] (w.r.t. a 4m long line)	+ 1.4	

Figure 3-2: Thermal Performance Assessment - Increase of Cold Gas Thruster Specific Impulse

In conclusion, for the configuration studied here, the cold gas thruster line with ACPB yields about 6% more specific impulse in average compared with the reference case without ACPB. This gain is at the cost of an additional mass of only 1.4kg by the ACPB for a 4m long line.

3.1.3 Requirements for the ACPB development

Based on the identified space applications in WP2100 development requirements for the ACPB development have been established.
A visualization of the requirements is shown in Figure 3-3.

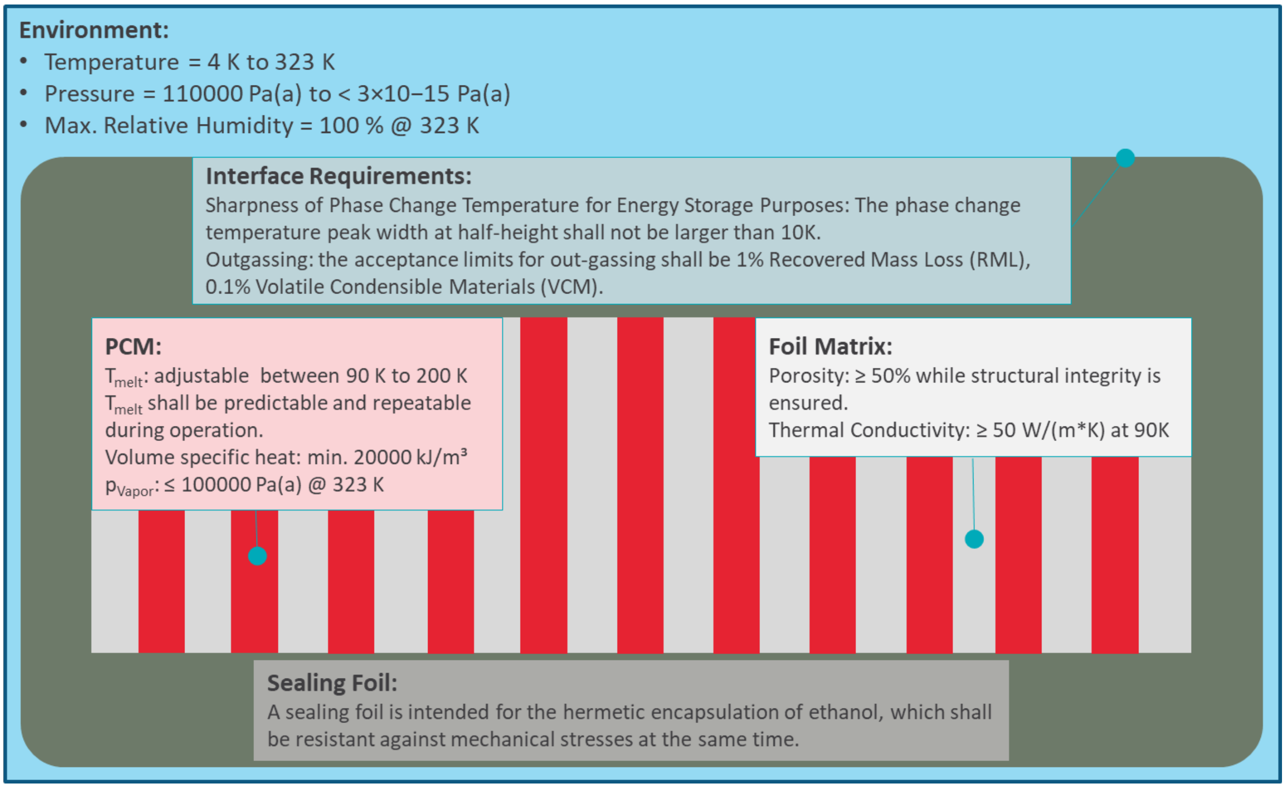


Figure 3-3: Visualization of the ACPB development requirements

For the demonstrator development the following requirements have been derived:

- Ethanol shall be used as PCM
- As a first proof of concept test, a freezing point depression of ethanol by 10K shall be targeted.
- The substrate of the ACPB shall have a porosity of ≥ 50% while structural integrity is ensured.
- The thermal conductivity of the ACPB matrix shall be ≥ 50 W/(m*K) at 90K.
- The PCM shall have a vapour pressure at 323K of ≤ 100000 Pa(a).

3.2 Molecular Dynamics Simulations

Covered Work packages: WP4100

Alongside with the DSC breadboard tests on a nanoporous sample the molecular dynamics simulations shall provide detailed insights on the effect of nanoscale confinement within pores on the liquid/solid phase transition of Ethanol. Thus the validity of the macroscopic description of the freezing point depression in cylindrical pores according to Gibbs-Thomson shall be proofed for nanopores.

3.2.1 Validity of the Gibbs-Thomson Equation for Nano-scale applications

The macroscopic description of the freezing point depression via Gibbs-Thomson equation is valid for the following assumptions

- Single component system.
- Only reversible processes.
- The curvature of the interface is unchanged during the phase transition.
- Pure phases with constant composition.
- No interface-effects such as preferential adsorption or molecular orientation at interfaces.
- No effects which invalidate a classical thermodynamic treatment, such as changes in thermodynamic properties due to finite size-effects
- No direct effect of pore-walls in cases where the curvature of the liquid/solid interface is due to liquid/pore-wall interactions such as contact-angle phenomena or capillary effects. The pore-walls only affect the contact angle of the liquid and thus the geometric term of the Gibbs-Thomson equation.

3.2.2 Results of the Molecular Dynamics Simulations

For pore-diameters greater than 50 nm any nano-scale effect is considered as negligible. For pore-diameters below 50 nm, an additional freezing-point depression of less than 2 K may be realizable due to an adsorbed surface layer on the pore walls.

At pore-diameters below 20 nm, a purely geometric argument shows that more than 35% of Ethanol molecules will be adsorbed at the surface. A thermodynamic assessment is then no longer possible.

3.2.3 Gibbs-Thomson Effect for Pore-Confined Ethanol

The expected freezing point depression for pore-confined ethanol according to the Gibbs-Thomson Equation is shown in Figure 3-4.

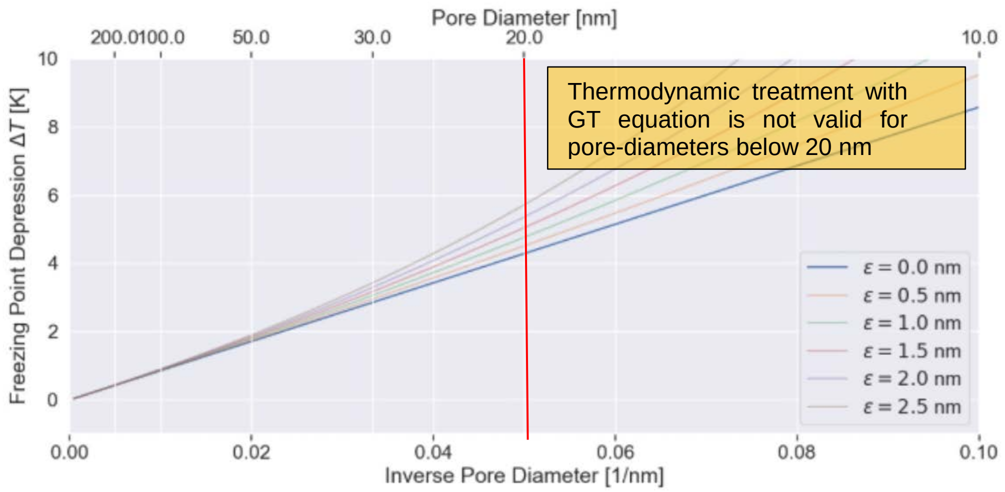


Figure 3-4: Freezing Point Depression from the modified Gibbs-Thomson Equation for Ethanol

As shown in Figure 3-4 freezing-point depressions in excess of 10 K are only achievable with very small pore diameters. For example a pore-diameter of 30 nm leads to a depression of only 3

K. We note here that a purely thermodynamic treatment is certainly not valid for 10 nm pores with 2 nm thick adsorption layers at the pore-walls due to finite-size effects.

3.3 DSC Breadboard Test with nanoporous AAO Membranes

Covered work packages: WP2300, WP5100, WP6100

Experimental proof of the freezing point depression of ethanol confined in nanoporous Anodic Aluminum Oxide substrates should have been given by DSC breadboard tests.
The two following types of AAO membranes, delivered by SmartMembranes GmbH, were examined.

- SmartPor 25 (Pore diameter 40-45 nm, Porosity 45%)
- SmartPor 180 (Pore diameter 335 nm, Porosity 45%)

In a first step the wetting behaviour of the membrane surface had to be evaluated. Therefore, the topographic properties of the membrane have been investigated by means of scanning electron microscopy (SEM), and the chemical composition of the membrane surface have been analysed using photoelectron spectroscopy (XPS).

The SEM images show a relatively homogeneous pore distribution. The measured pore diameters correspond approximately to the nominal values.

The XPS results are interpreted, that in both cases the membrane surfaces are clean enough to enable a completely wetting with ethanol. Low carbon concentrations as well as residues of sulfur and phosphorus are not expected to influence the wetting of the membrane surfaces with ethanol.

3.3.1 Results of the DSC measurements

The results of the DSC measurements are summarized in

Table 3-1

Table 3-1: Measured freezing point of ethanol within membrane pores and of ethanol in reference state

Sample	Freezing point / °C
Ethanol reference (bulk)	-118,5
Ethanol-filled SmartPor 25	incapable of measurement
Ethanol-filled SmartPor 180	-118,7
Ethanol-filled aluminum membrane with pore diameter 100 nm	-118,0

The DSC data show that there is no significant difference between the ethanol within the SmartPor 180 membrane (pore diameter 330 nm) and the aluminum membrane (pore diameter 100 nm) on the one side and the ethanol reference sample on the other side concerning their freezing points. So obviously the confinement of ethanol in nanopores down to a pore diameter of 100 nm does not lead to any freezing point depression.

In case of the membrane SmartPor 25, no phase transition could be measured at all, even though the quantity of ethanol within the pores was verified by exact weighting.
For this behaviour several reasons are imaginable:

- Absence of a sufficient number of nucleation sites as starting points for the phase transition.
- Macroscopic thermodynamic descriptions are not applicable due to a manageable number of ethanol molecules.

3.4 Thermal Performance Test

Covered work packages: WP2300, WP5200, WP6200

Thermal performance of the ACPB has been investigated with a guarded hot-plate apparatus in a thermal vacuum test according to the following sequence (derived from ASTM C177 and ISO 8302):

- During the tests the vacuum level in the chamber has been < 0.0001 mbar.
- The cold plates have been cooled to 77 K with LN2 during all test phases.
- Cool-down: the de-activated main heater and the guarded heater have been cooled down to a temperature < 125 K
- Both heaters have been activated once the < 125 K premise has been reached. Heater power has been adjusted through duty cycling and regulation of the guard heater until a temperature of 154 K (steady state) has been reached on the both heaters.
- Slowly passing through the phase transition of Ethanol with constant heater power, which has been derived from the heater power to maintain steady state conditions at 154 K.

A test prediction has been performed by thermal analysis with ESATAN.

3.4.1 Test Sample Description

For the thermal performance test 10 samples have been manufactured. Each sample has a size of 300mm x 300mm. It consists of a 100µm thick, perforated aluminum foil with a porosity of 50%. Ethanol is filled in the open pores and everything is sealed mechanical afterwards with 10µm thick aluminum foils from both sides.

Due to the low maturity level of the sealing concept in this early stage of the ACPB development additional sealing by means of a weldable barrier foil of about 110µm in thickness has been required. The layer composition of the test samples is shown in Figure 3-5.

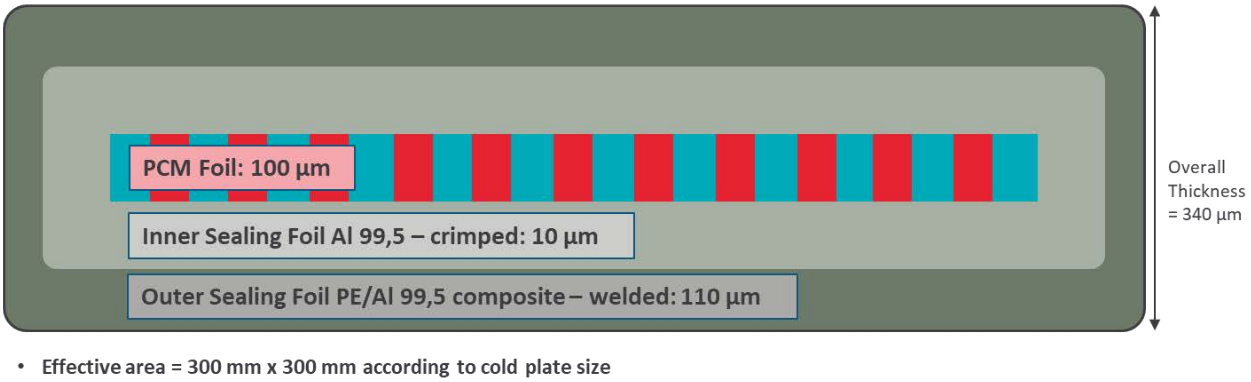


Figure 3-5: PCM Blanket Design for Thermal Performance Test

With this additional sensible heat of the outer bag, the ratio of latent heat to the overall sensible heat would have otherwise been too small. Thus, ethanol was overfilled in order to keep the ratio of latent heat to sensible heat reasonably high. The average ratio of the PCM to the sealing foils for the test samples is shown in

Table 3-2.

Table 3-2: Average ratio PCM to sealing foils for the test samples

	Average Weight	Weight%
	g	%
Blanket	79,25	
Sealing Foils	51,70	65%
PCM Ethanol	27,56	35%

3.4.2 Thermal Performance Test Results

In the frame of the thermal performance tests the vacuum tightness of the blankets has been verified. For this achievement an additional sealing layer has to be used, as can be seen in Figure 3-5.

Due to residual gas inside the ACPB test samples no clear indication of a phase change could be detected during the thermal performance tests under vacuum conditions, most probably due to a ballooning effect of the blankets.

An additional test was conducted in a dry nitrogen atmosphere under atmospheric pressure. The same blankets were used, since no other encapsulation process with less remaining gas in the blanket could be realized in this time frame.

The measured temperature trends during the test under atmospheric conditions seem to show an indication for a phase change.
It is expected that high blanket internal thermal resistances are the main reason for the washed out temperature signal during the phase change. These are caused by the double sealing as shown in Figure 3-5.

3.4.3 Test Correlation – Thermal Performance Test

A test correlation via TMM has been used to explain the difficulties to detect the phase change. Therefore the TMM, which has been used for the test prediction, was modified.

A set of interface conductances was considered in between each layer to take the blanket internal thermal resistances into account. Automatic correlation has been used to make well founded assumptions for the conductance values.

With the correlated interface conductances a very good agreement between the TMM and the test data has been achieved at the start of the transient phase of passing through the phase change of one blanket, as can be seen in Figure 3-6.

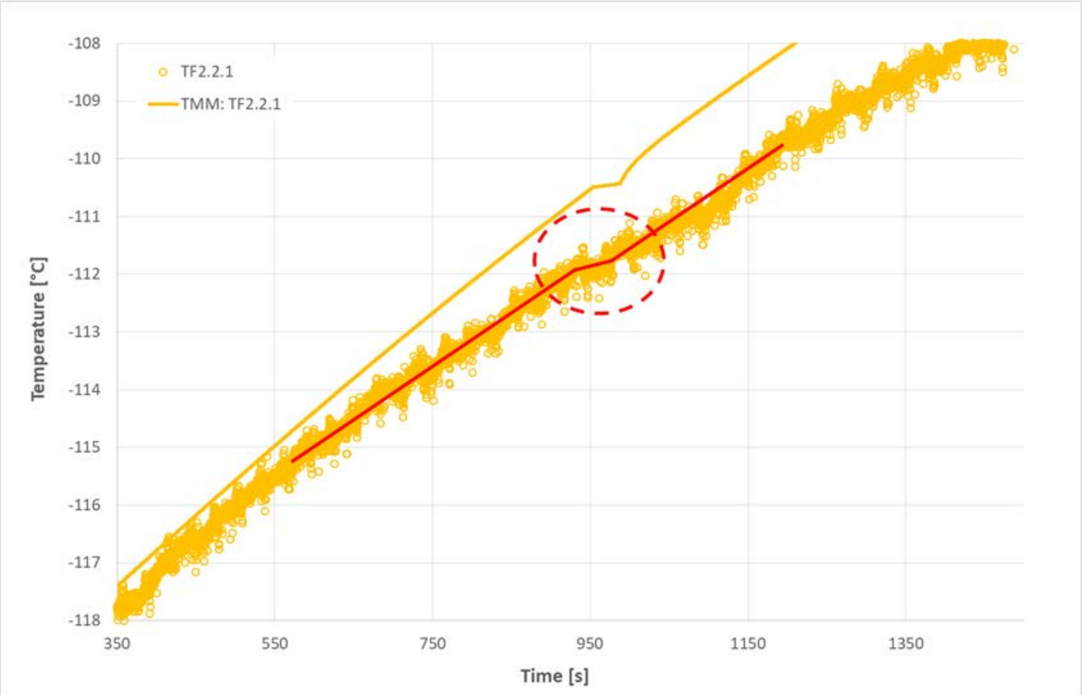


Figure 3-6: Comparison Experiment and Correlated TMM

A close look to the TF2.2.1-evolution in Figure 3-6 reveals a temperature slope discontinuity attributed to a phase change about 1.5 °C higher in the simulation compared to the measurement. Also the indication of the phase change in the test data at about -112 °C is still about 1.5 °C warmer than the normal melting point of ethanol. This can be explained now by the model as a result of the blanket-internal interface resistance between the inner and the outer bag.

3.4.4 Refined Test Prediction without Blanket Internal Resistance

A refined test prediction has been performed with the following assumptions:

- High interface conductances of 1000 W/K between the blankets, which could be achieved e.g. by gluing.
- No blanket internal interface resistance, which could be achieved if the ethanol filling and encapsulation process is completely gas-free.

The modified TMM from the Thermal Performance Test correlation has been used.
As can be seen in Figure 3-7, which shows the predicted temperature trend on the contact surface between the heater's nearest blanket and the heater, the phase change at the normal melting point of ethanol at -114.5°C should be detectable.

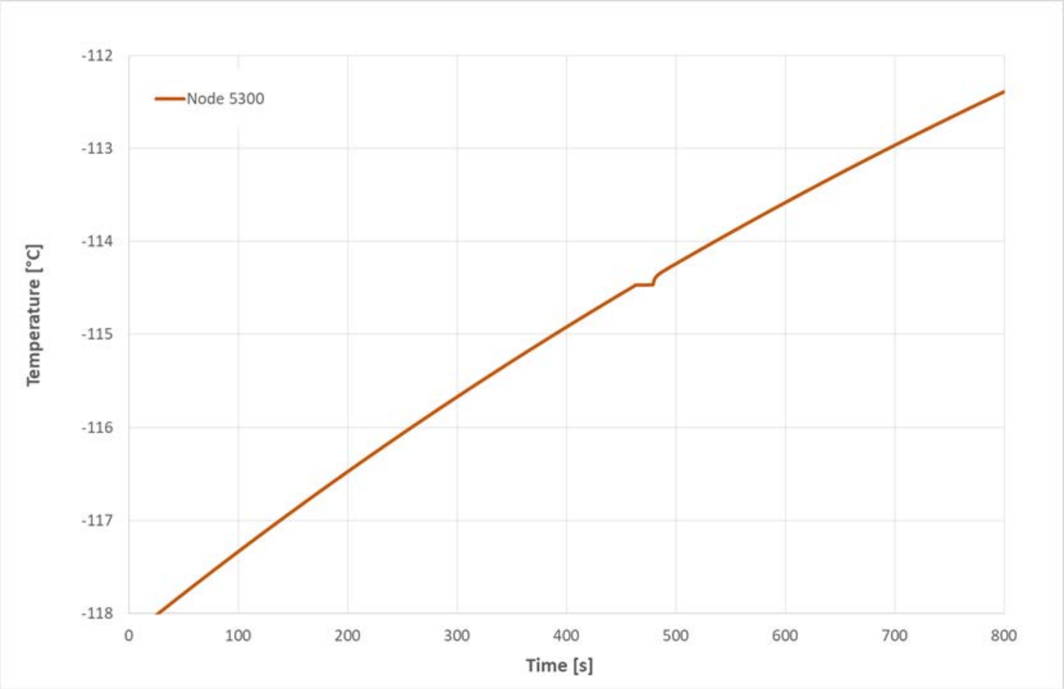


Figure 3-7: Test prediction without blanket internal resistance: Passing through phase change of heater's nearest blanket

4 Conclusions

Based on the results of this de risking activity, it can be concluded that the use of ethanol-filled cryo-PCM blankets is possible for space applications.
It could be demonstrated that ethanol can be safely stored between the foils and withstands the stresses caused under vacuum conditions.
For the development of future thermal hardware, which is based on this technology, it is to make sure that the blankets are filled gas-free in order to achieve a high thermal performance. Suitable technologies must be identified for this process, the optimal structure of the blankets and the choice of materials must be determined and verified.

The performed investigations during this de-risking activity comprise theoretical and experimental work content.
At first, ten applications for Adjustable Cryo PCM Blankets (ACPB) on spacecrafts have been identified, some for already existing technologies like solar cells, others for speculative technologies in the future like High Temperature Superconductors.
The two out of five most promising applications identified for launchers have been taken for detailed thermal assessments with a Thermal Mathematical Model.
It has been shown that the electrical output of solar cells mounted on a Launcher Upper Stage could be increased by about 11% due to application of the ACPB, while the additional mass by the ACPB increased only slightly.
In the second assessment it has been demonstrated that the specific impulse of cold gas thrusters can be increased by about 6% at a negligible additional mass of ACPB.

As a key feature of the proposal for the performed de-risking activity the freezing point depression of a PCM confined in nanopores according to Gibbs-Thomson has been investigated by Molecular Dynamics Simulations and DSC Breadboard Tests.
The theoretical investigations and MD simulations have shown that the feasible freezing point depression in nanopores is not as high as expected. Very small pore sizes of diameters smaller than 10 nm are required to achieve the freezing point depressions, which are required e.g. by the identified and analysed space applications. MD simulations have shown that a prediction of the freezing point depression in this pore-size range (≤ 10 nm) is not reliable due to molecular effects.
These findings are supported by the DSC breadboard tests, which have shown no detectable freezing point depression at all for nanopores with pore diameters with 40 nm.
In conclusion it is a key finding of this de-risking activity that adjustment of the freezing point by utilization of the Gibbs-Thomson effect is not feasible in the expected scope of application.

Thermal performance of exemplary ACPB test samples without freezing point depression has been investigated by test. Due to the low maturity grade of the sealing concept at the current state of the ACPB development, tightness has been ensured by a double layer of sealing foils.
This induced several issues such as increased thermal interface resistances as well as high blanket-internal thermal resistances to the experimental proof of the ACPB thermal performance.
Under vacuum conditions the effect of the latent thermal storage medium could not be detected.
A second test under atmospheric conditions with dry nitrogen atmosphere has shown an indication for a phase change, which has been confirmed within a model correlation.

Blanket-internal thermal resistance is assumed to be overcome by a complete gas-free ethanol filling and encapsulation process. Furthermore the interface resistances between the ACPB in multi-layer configuration are expected to be reduced by gluing at the interface surfaces.
Thermal analysis for the performance prediction of future blankets with zero blanket internal thermal resistances and decreased thermal interface resistances show easy to detect phase changes of each blanket.

5 Further Study Areas

The following way forward is proposed by the participants of this de-risking activity:

Due to the advantageous properties of ethanol with respect to the ACPB requirements it is proposed by the participants of this de-risking activity to proceed with eutectic mixtures with ethanol as one ingredient to reach the required freezing points as identified for the space applications.

Based on the findings of the thermal performance test further efforts are required on the design and the arrangement of the ACPB.
A suitable concept for evacuation, filling and sealing of the blankets needs to be developed. For example a small fill/drain connection in form of a nipple at the ACPB edge is thinkable. As derived from the thermal performance test results the ethanol filling and encapsulation process shall be completely gas-free.

Thermal performance assessments of possible space applications have given an expectation of the required amount of PCM for the respective case. For example a total ACPB thickness of 1.5 mm excluding the sealing foil is required for the solar-cell application, which would result in a multilayer arrangement of 15 blankets. According to the results of the thermal performance test multilayer arrangement induces further challenges due to e.g. thermal interface resistances.
It needs to be investigated which arrangement of the ACPB is favourable in terms of performance while remaining the advantages in mechanical integration due to being a flexible blanket.