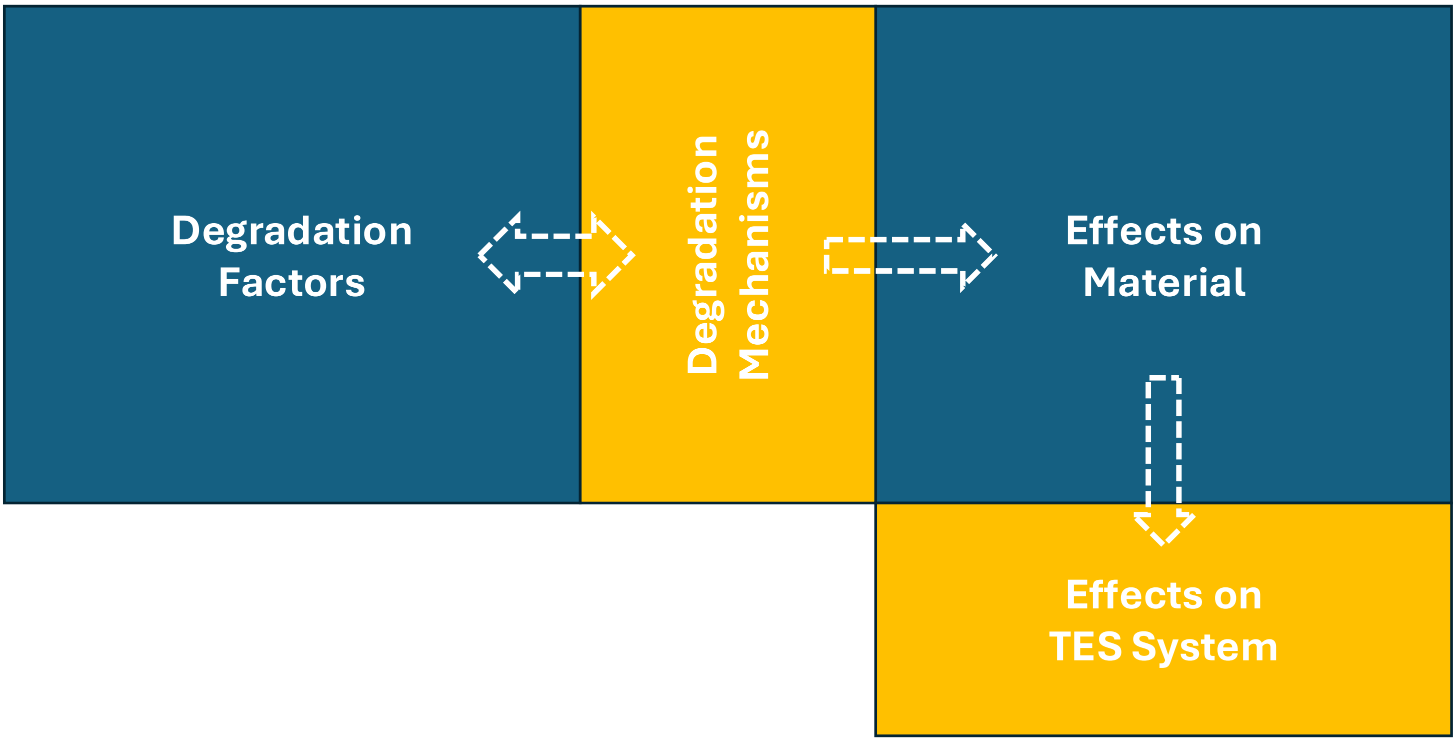
SOLAR HEATING & COOLING PROGRAMME
INTERNATIONAL ENERGY AGENCY

Mapping degradation of PCM and TCM

Subtask D



IEA SHC TASK 67 | Compact thermal Energy Storage Materials within Components within Systems

Technology Collaboration Programme
by iea

Subtask D

Mapping degradation of PCM and TCM

This is a report from SHC Task 67: | Compact thermal Energy Storage Materials within Components within Systems

and work performed in Subtask D: Stability of PCM and TCM

Author: Christoph Rathgeber
Date September 2025
Report number, DOI: 10.18777/ieashc-task67-2025-0001

Solar Heating & Cooling Technology Collaboration Programme (IEA SHC)

The Solar Heating and Cooling Technology Collaboration Programme was founded in 1977 as one of the first multilateral technology initiatives ("Implementing Agreements") of the International Energy Agency.

Our mission is *to bring the latest solar heating and cooling research and information to the forefront of the global energy transition.*

IEA SHC members carry out cooperative research, development, demonstrations, and exchanges of information through Tasks (projects) on solar heating and cooling components and systems and their application to advance the deployment and research and development activities in the field of solar heating and cooling.

Our focus areas, with the associated Tasks in parenthesis, include:

- Solar Space Heating and Water Heating (Tasks 14, 19, 26, 44, 54, 69)
- Solar Cooling (Tasks 25, 38, 48, 53, 65)
- Solar Heat for Industrial and Agricultural Processes (Tasks 29, 33, 49, 62, 64, 72)
- Solar District Heating (Tasks 7, 45, 55, 68)
- Solar Buildings/Architecture/Urban Planning (Tasks 8, 11, 12, 13, 20, 22, 23, 28, 37, 40, 41, 47, 51, 52, 56, 59, 63, 66)
- Solar Thermal & PV (Tasks 16, 35, 60)
- Daylighting/Lighting (Tasks 21, 31, 50, 61, 70)
- Materials/Components for Solar Heating and Cooling (Tasks 2, 3, 6, 10, 18, 27, 39)
- Standards, Certification, Test Methods and LCA/LCoH (Tasks 14, 24, 34, 43, 57, 71)
- Resource Assessment (Tasks 1, 4, 5, 9, 17, 36, 46)
- Storage of Solar Heat (Tasks 7, 32, 42, 58, 67)

In addition to our Task work, other activities of the IEA SHC include our:

- SHC Solar Academy
- *Solar Heat Worldwide*, annual statistics report
- SHC International Conference

Our members

Australia
Austria
Belgium
Canada
CCREEE
China
Denmark
EACREEE
ECREEE
European Commission
France
Germany
International Solar Energy Society
Italy
Netherlands
Norway
Poland
Portugal
RCREEE
SACREEE
SICREEE
Slovakia
South Africa
Spain
Sweden
Switzerland
Türkiye
United Kingdom

For more information on the IEA SHC work, including many free publications, please visit www.iea-shc.org.

Contents

1 Contributors

This report was written by Christoph Rathgeber (ZAE Bayern, Germany). The content of this report was provided from Ángel Serrano (CIC energiGUNE, Spain), Rocio Bayón (CIEMAT, Spain), Rebecca Ravotti (HSLU, Switzerland), Emanuela Mastronardo (Univ. of Messina, Italy), Henri Schmit (ZAE Bayern, Germany), Louis Desgrosseilliers (SPF, Switzerland), Henk Huinink (TU Eindhoven, The Netherlands), Lia Kouchachvili (CanmetENERGY, Canada), and their research teams.

Further participants in Subtask D were Gayaneh Issayan and Bernhard Zettl (Univ. of Applied Science Upper Austria), Peter Weinberger, Frieda Kapsamer, Jakob Smith, and Jakob Werner (TU Vienna), Wim van Helden (AEE Intec, Austria), Reda Djebbar and Dylan Bardy (CanmetENERGY, Canada), Handan Tezel (Univ. of Ottawa, Canada), Dominic Groulx (Dalhousie Univ., Canada), Alireza Afshari, Evdoxia Paroutoglu, and Allesandro Maccarini (Aalborg Univ., Denmark), Gerald Englmair and Jianhua Fan (DTU, Denmark), Nolwenn Le Pierrès, Michel Ondarts, Jonathan Outin, and Elise Berut (Univ. Savoie Mont Blanc, France), Grégory Largiller (CEA, France), Franziska Klünder, Sebastian Gamisch, and Stefan Gschwander (Fraunhofer ISE, Germany), Simon Pöllinger (ZAE Bayern, Germany), Ruud Cuypers (TNO, The Netherlands), Alenka Ristić (NIC, Slovenia), Inés Fernández and Camila Barreneche (Univ. of Barcelona, Spain), Gabriel Zsembinszki, Emiliano Borri, David Verez and Luisa F. Cabeza (Univ. of Lleida, Spain), Yulong Ding, Helena Navarro, and Anabel Palacios Trujillo (Univ. of Birmingham, UK), Jonathon Elvins (Swansea Univ., UK), and Carolina Costa (Northumbria Univ., UK).

2 Introduction and Objectives

2.1 Investigating CTES material stability

What is meant by material stability of compact thermal energy storage (CTES) materials? A general definition could be: A CTES material is stable if its relevant properties (e. g. melting/reaction enthalpy and temperature, chemical composition, etc.) remain unchanged within a certain limit (compared to the initial state) during and after testing. Testing can refer to both laboratory tests and monitoring of the CTES material within an energy storage system.

Therefore, to talk about CTES material stability, it is necessary to know or investigate the processes that lead to a CTES material no longer being stable. In the context of this Task, these processes are referred to as degradation mechanisms.

Different degradation mechanisms are to be considered when studying CTES material stability. For example, chemical degradation of organic phase change materials (PCM) at high temperatures (Figure 2.1-1, left) or breaking up zeolite pellets by hydrothermal aging (Figure 2.1-1, right).

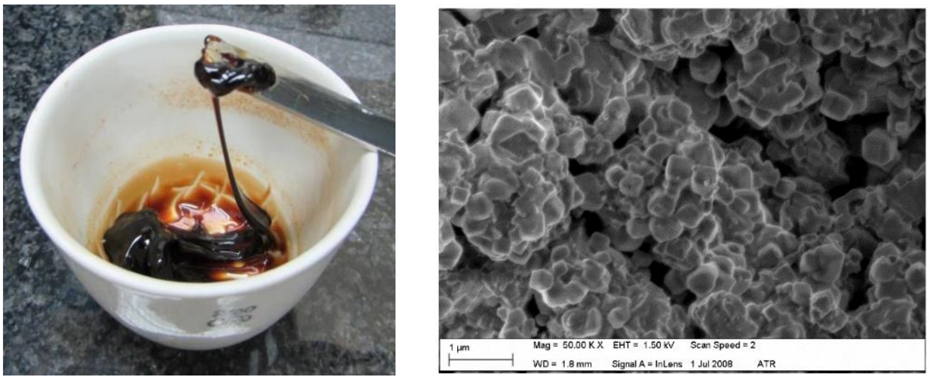


Figure 2.1-1: Examples for degradation of PCM (left: thermal decomposition of D-mannitol, a sugar alcohol [1]) and thermochemical materials (TCM) (right: breaking up zeolite pellets by hydrothermal aging [2]).

In the previous SHC Task 58 / ES Annex 33, one topic was testing PCM under application conditions. This included an inventory of properties of PCM that change comparing lab-scale experiments with tests under application conditions, and a paper on experimental devices and techniques to investigate degradation of PCM [3]. Both deliverables pointed to the relevance of investigating the stability of PCM. It became obvious that the stability of PCM, as a key requirement for a successful development and commercialisation of latent heat thermal energy storage systems, strongly depends on the material (class) and the applied testing conditions. This means that no general statement of the type "Material xy is stable." or "Material xy is not stable." can be made without reporting the specific testing conditions.

The state of scientific literature with respect to the stability of PCM can be illustrated with three representative papers. The first paper is exemplary for many similar publications: a review paper on tested CTES materials (in this case PCM) and applied experimental methods. Ferrer et al. [4] reported on thermally cycled PCM of different material classes (including organic and inorganic materials). They prepared extensive tables with data for initial (before cycling) and final (after cycling) material properties and indicated the applied test method. In addition, they listed the experimental devices including information on the manufacturer and device type used by different authors.

The second paper proposes a methodology for a step-by-step validation of CTES materials, exemplary applied to a sugar alcohol used as PCM. With validation, Bayón and Rojas [5] mean testing and verifying the long-term stability and long-term performance of a material. They state that “no testing protocol or guideline exists up to now for validating storage media, so that authors apply their own criteria, not only for designing testing procedures but also for predicting the material behaviour under long-term operation.” Their proposed “methodology consists of different stages that include PCM characterization, preliminary assessment tests, and accelerated life testing.” Overall, their method has a strong focus on considering application conditions (called “service conditions”) when testing the stability. To perform accelerated tests – which are expected to provide a faster assessment of the stability of a material – it is crucial to, first, know the relevant degradation factors (e.g. high-temperature, oxygen atmosphere, etc.) and, second, perform “tests under increasing stress level of degradation factors” (e.g. higher temperatures than those to which the CTES material is normally exposed). As an example, they choose D-mannitol, a sugar alcohol, to illustrate their methodology. Among others, they evaluate “lifetime relationship diagrams for the thermal degradation of D-mannitol” showing the reduction in melting enthalpy obtained after exposure to different static temperatures (between 170 and 210 °C).

In the third paper, Mehling [6] presents a systematic approach to investigate property degradation of PCM. He emphasizes that “as different applications impose different conditions […], testing should be tailored to the individual case”. According to his method, “first the basic functions and related properties that might be subject to testing, e.g., with a specific application in mind” are to be identified. Following this, the method proposes an “approach to find the degradation effects and underlying mechanisms to allow tailoring and optimizing test procedures”. The paper demonstrates the approach for the function of heat storage of PCM.

Overall, these three papers span the current state of research into the stability of PCM. Similar papers can be found for TCM. There is a lot of data available, often with little background information on the experimental boundary conditions of testing. At the same time, there are suggestions for a structured approach to investigating stability, considering the specific application.

Based on the outlined state of literature and the work from the previous Task 58 / Annex 33, the SHC Task 67 / ES Task 40 experts have derived the following objectives for Subtask D.

2.2 Objectives

The main goal of Subtask D was to come to a better understanding of the stability of PCM and TCM and, thereby, derive recommendations for an application-oriented stability testing. Previous works and the state of literature lack of (I) sorting and differentiating the relevant degradation mechanisms, (II) showing which test methods are suitable for determining the respective degradation, and (III) making (material class-specific) recommendations for accelerating the measurements.

The two objectives to work towards this goal were:

1. Mapping degradation mechanisms for CTES material classes
2. Come up with recommendations for stability testing
    a. …based on simple experiments
    b. …to faster investigate stability by accelerating degradation

In the following, the development of a degradation mapping table covering these objectives will be presented.

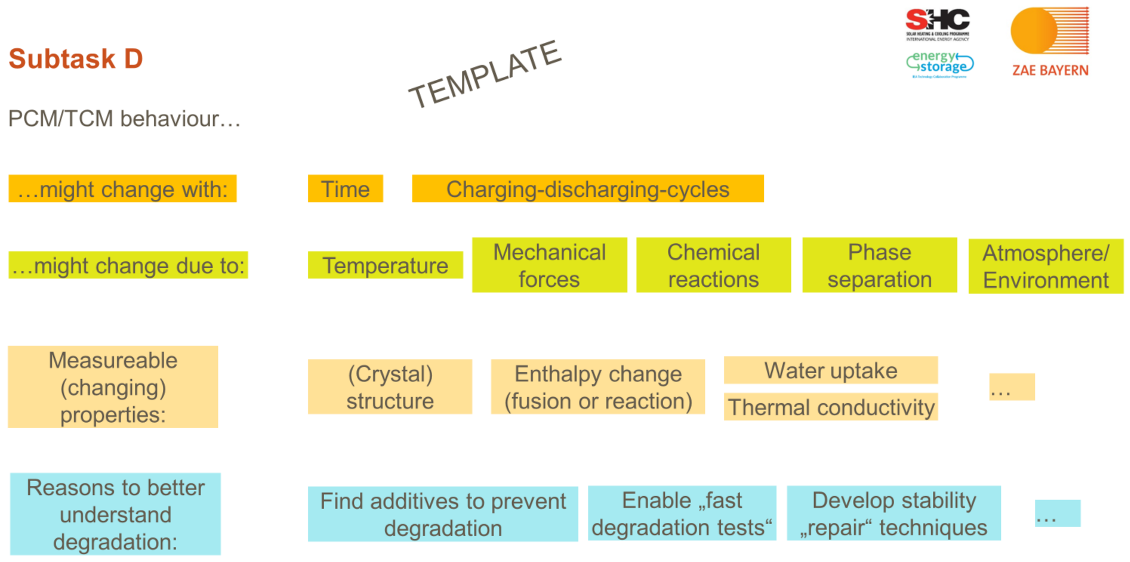
3 Mapping of CTES material degradation

3.1 Motivation

CTES material degradation mapping should provide an easy-to-read and comprehensive overview that directly shows the relationships between test conditions, degradation mechanisms, and effects on the material and, if tested, the CTES system. In the course of the Task, several visualization approaches were proposed, discussed, and further refined. Common to all approaches was the ambition to sort and structure discussions on stability, insofar as different questions and perspectives should be included in such a mapping: What are the reasons for degradation? What are the effects of degradation on the material (properties)? How can degradation be identified and quantified? How to accelerate degradation to accelerate the testing?

3.2 Visualization approaches

Figure 3.2-1 is an attempt towards such a structuring. A distinction (lines of different colours) is made between what CTES material behaviour might change with, what it might change due to, measurable properties to assess that change, and reasons to better understand the degradation. This structuring was proposed and discussed at the early expert meetings.



Subtask D

TEMPLATE

PCM/TCM behaviour…

…might change with: Time | Charging-discharging-cycles

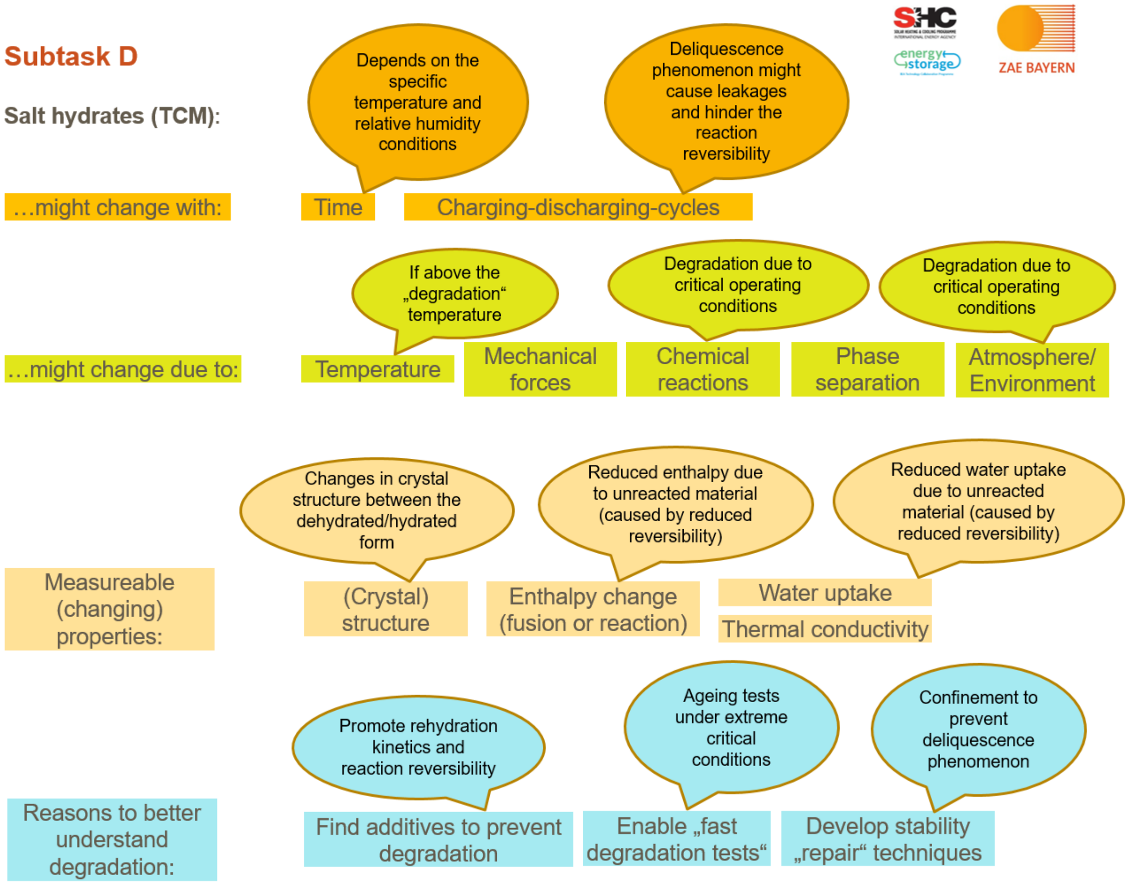
…might change due to: Temperature | Mechanical forces | Chemical reactions | Phase separation | Atmosphere/ Environment

Measureable (changing) properties: (Crystal) structure | Enthalpy change (fusion or reaction) | Water uptake | Thermal conductivity | …

Reasons to better understand degradation: Find additives to prevent degradation | Enable „fast degradation tests“ | Develop stability „repair“ techniques | …

Figure 3.2-1: First approach to structure CTES material stability.

The template was distributed among the Task experts with CTES material stability knowledge. Task experts were asked to add their comments to the template to provide an overview of the stability behaviour of the CTES material (class) they have experience with. As an example, Figure 3.2-2 shows the template filled in for salt hydrates to be used as TCM.



Subtask D

Salt hydrates (TCM):

…might change with: Time; Charging-discharging-cycles

- Time: Depends on the specific temperature and relative humidity conditions
- Charging-discharging-cycles: Deliquescence phenomenon might cause leakages and hinder the reaction reversibility

…might change due to: Temperature; Mechanical forces; Chemical reactions; Phase separation; Atmosphere/ Environment

- Temperature: If above the „degradation“ temperature
- Chemical reactions: Degradation due to critical operating conditions
- Atmosphere/ Environment: Degradation due to critical operating conditions

Measureable (changing) properties: (Crystal) structure; Enthalpy change (fusion or reaction); Water uptake; Thermal conductivity

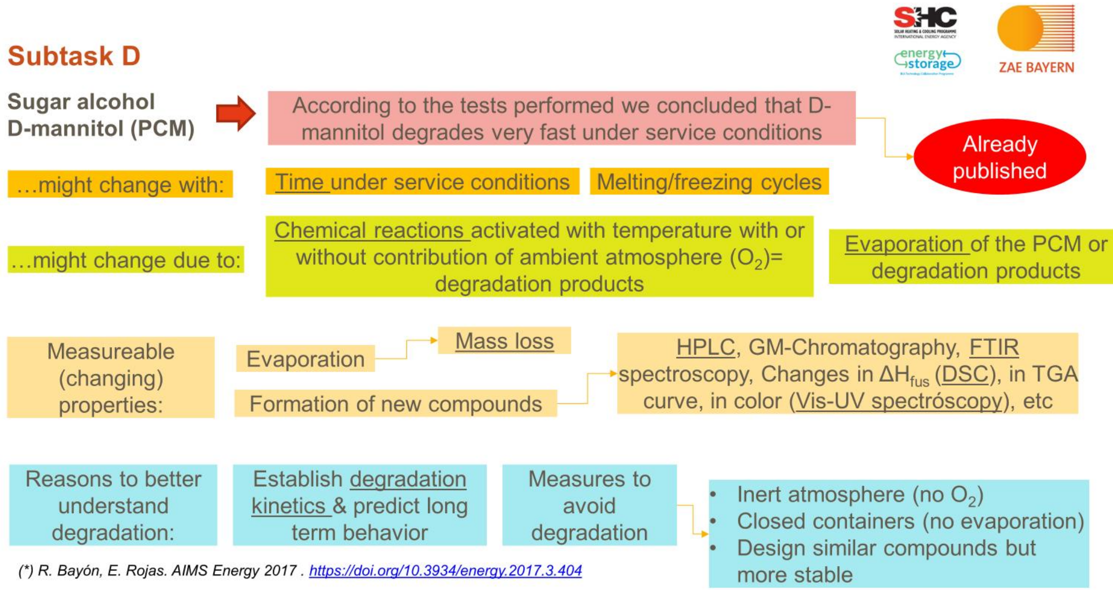
- (Crystal) structure: Changes in crystal structure between the dehydrated/hydrated form
- Enthalpy change (fusion or reaction): Reduced enthalpy due to unreacted material (caused by reduced reversibility)
- Water uptake: Reduced water uptake due to unreacted material (caused by reduced reversibility)

Reasons to better understand degradation: Find additives to prevent degradation; Enable „fast degradation tests“; Develop stability „repair“ techniques

- Find additives to prevent degradation: Promote rehydration kinetics and reaction reversibility
- Enable „fast degradation tests“: Ageing tests under extreme critical conditions
- Develop stability „repair“ techniques: Confinement to prevent deliquescence phenomenon

Figure 3.2-2: First approach to structure CTES material stability filled in for salt hydrates as TCM (source: Univ. Messina).

A modification of this presentation type was proposed by Rocio Bayón of CIEMAT, Spain (Figure 3.2-3).



Subtask D

Sugar alcohol D-mannitol (PCM) → According to the tests performed we concluded that D-mannitol degrades very fast under service conditions → Already published

…might change with: Time under service conditions; Melting/freezing cycles

…might change due to: Chemical reactions activated with temperature with or without contribution of ambient atmosphere (O_2)= degradation products; Evaporation of the PCM or degradation products

Measureable (changing) properties:

- Evaporation → Mass loss
- Formation of new compounds → HPLC, GM-Chromatography, FTIR spectroscopy, Changes in ΔH_{fus} (DSC), in TGA curve, in color (Vis-UV spectróscopy), etc

Reasons to better understand degradation: Establish degradation kinetics & predict long term behavior; Measures to avoid degradation →

- Inert atmosphere (no O_2)
- Closed containers (no evaporation)
- Design similar compounds but more stable

(*) R. Bayón, E. Rojas. AIMS Energy 2017 . https://doi.org/10.3934/energy.2017.3.404

Figure 3.2-3: Second approach to structure CTES material stability filled in for D-mannitol as PCM (source: CIEMAT).

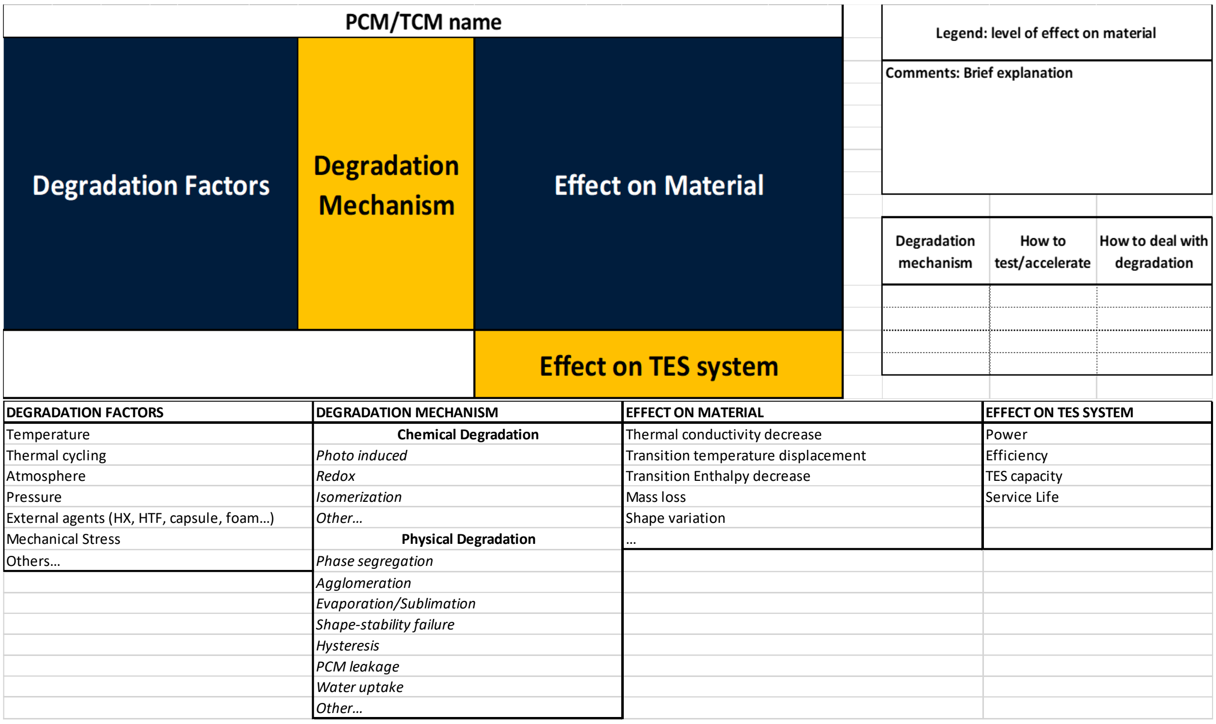
It adapts the presentation type specifically to the selected material class, links the relevant degradation mechanisms to appropriate experimental investigation methods, adds a conclusion on stability according to the investigation conditions applied and refers to a corresponding publication (if available).

A third type of presentation was developed by Ángel Serrano of CIC energiGUNE, Spain. This approach connects the degradation mechanisms (e.g. phase separation, corrosion, polymorphism) with their effect on the CTES material (e.g. change in transition enthalpy or thermal conductivity) and the performance on system level (e.g. change in power or capacity). The degradation mechanisms are in turn specified in more detail by their dependence on application conditions, in this approach called “degradation factors” (e.g. temperature, thermal cycling, atmosphere, etc.).

The template shown in Figure 3.2-4 is divided into a table with

a) Degradation factors
b) Degradation mechanisms
c) Effect on the material
d) Effect on the TES system

In addition, the template provides a box to leave a brief summary comment, along with a table that gathers information on how to test/ accelerate the selected degradation mechanisms and how to deal with this degradation.



Legend: level of effect on material

Comments: Brief explanation

Degradation mechanism	How to test/accelerate	How to deal with degradation

DEGRADATION FACTORS	DEGRADATION MECHANISM	EFFECT ON MATERIAL	EFFECT ON TES SYSTEM
Temperature	**Chemical Degradation**	Thermal conductivity decrease	Power
Thermal cycling	*Photo induced*	Transition temperature displacement	Efficiency
Atmosphere	*Redox*	Transition Enthalpy decrease	TES capacity
Pressure	*Isomerization*	Mass loss	Service Life
External agents (HX, HTF, capsule, foam...)	*Other...*	Shape variation	
Mechanical Stress	**Physical Degradation**	...	
Others...	*Phase segregation*		
	Agglomeration		
	Evaporation/Sublimation		
	Shape-stability failure		
	Hysteresis		
	PCM leakage		
	Water uptake		
	Other...		

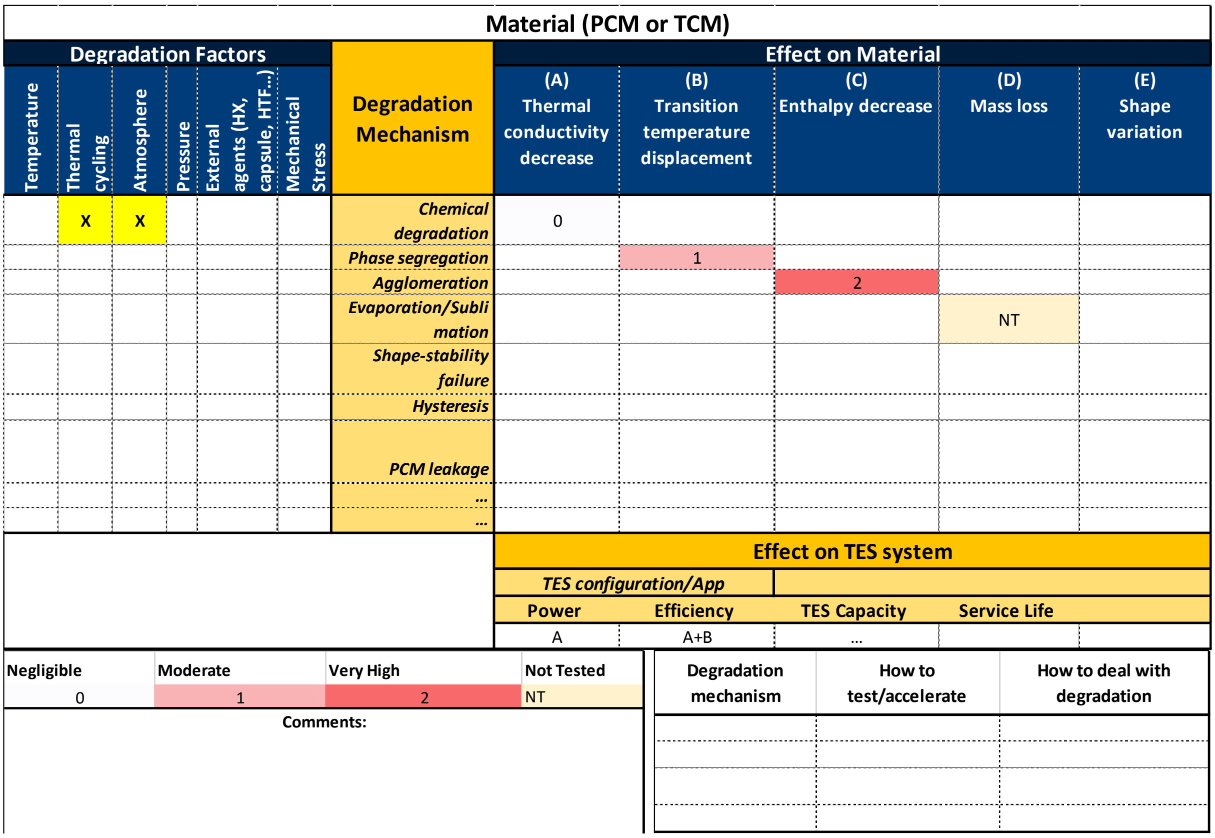
Figure 3.2-4: Explanation of the third approach’s template to structure CTES material stability.

The backbone of the document is the table with degradation mechanisms. Therefore, experts first indicate those degradation mechanisms that affect the material based on their experience. Second, an "X" marks those degradation factors that trigger the degradation mechanism. Third, the effect of this degradation mechanism on the PCM/TCM material is rated as 0 (negligible), 1 (moderate), 2 (very high), or NT (not tested).

The effect on the TES system typically depends on various factors, such as the TES system configuration or the application. In the template, the effect on the TES system is indicated through letters A, B, etc., which correspond to the different "Effects on Material".

Finally, experts may add a brief summary of the stability of the investigated CTES material, testing options for the degradation mechanisms, and proposals for dealing with the degradation (if possible and known).

The actual template that was shared with the Task experts is Excel-based. A screenshot of the template is given in Figure 3.2-5.



Material (PCM or TCM)

Degradation Factors						Degradation Mechanism	Effect on Material				
Temperature	Thermal cycling	Atmosphere	Pressure	External agents (HX, capsule, HTF...)	Mechanical Stress		(A) Thermal conductivity decrease	(B) Transition temperature displacement	(C) Enthalpy decrease	(D) Mass loss	(E) Shape variation
	X	X				*Chemical degradation*	0				
						Phase segregation		1			
						Agglomeration			2		
						Evaporation/Sublimation				NT	
						Shape-stability failure					
						Hysteresis					
						PCM leakage					
						...					
						...					

Effect on TES system

TES configuration/App				
Power	Efficiency	TES Capacity	Service Life	
A	A+B	...		

Negligible	Moderate	Very High	Not Tested
0	1	2	NT

Comments:

Degradation mechanism	How to test/accelerate	How to deal with degradation

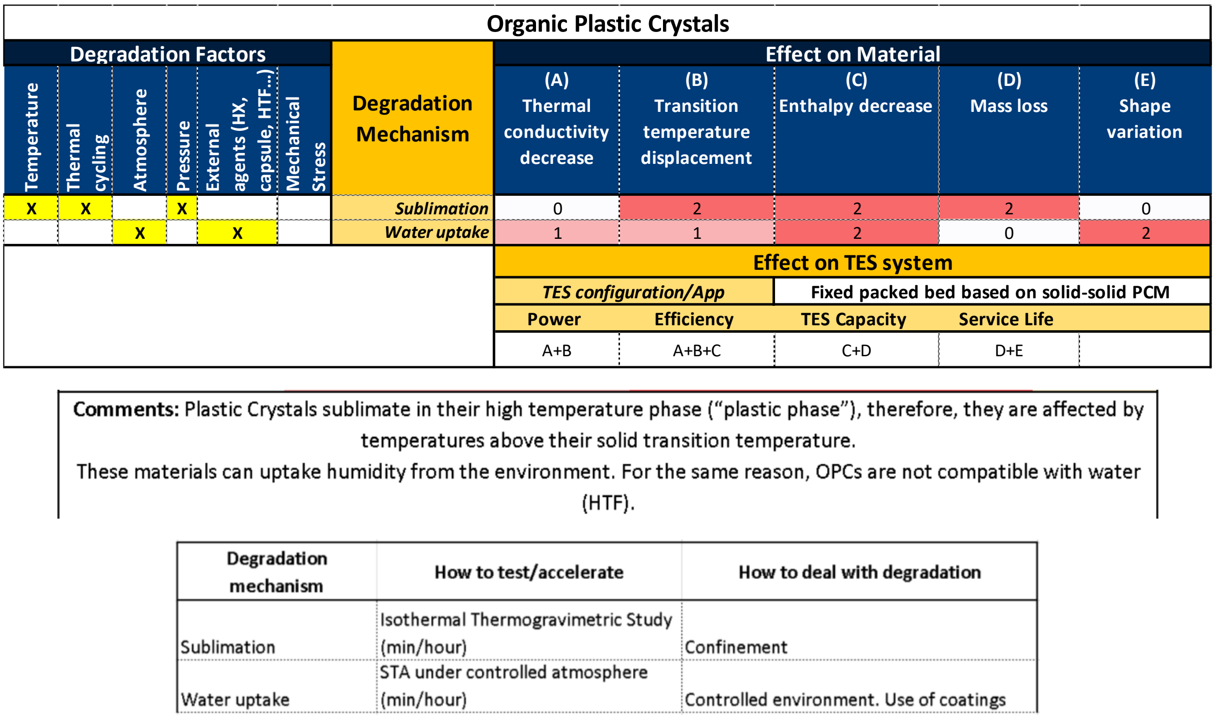
Figure 3.2-5: Third approach's template to structure CTES material stability.

3.3 Degradation mapping tables

In the following, some of the received examples of the third and final approach (cf. Figure 3.2-4 and Figure 3.2-5) to map CTES material degradation are given. The subsection headings contain the name of the CTES material or material class and if it is used as PCM or TCM. The sources of information are indicated in the figures' captions. The effect of a degradation mechanism on the material is rated as 0 (negligible), 1 (moderate), 2 (very high), or NT (not tested).

It is important to be aware that these tables do not contain all the knowledge available in the literature on material degradation but represent the corresponding expert's conclusions on the degradation behaviour of a particular material (class).

3.3.1 Organic plastic crystals (PCM)



Organic Plastic Crystals

Degradation Factors						Degradation Mechanism	Effect on Material				
Temperature	Thermal cycling	Atmosphere	Pressure	External agents (HX, capsule, HTF...)	Mechanical Stress		(A) Thermal conductivity decrease	(B) Transition temperature displacement	(C) Enthalpy decrease	(D) Mass loss	(E) Shape variation
X	X		X			*Sublimation*	0	2	2	2	0
		X		X		*Water uptake*	1	1	2	0	2

Effect on TES system

TES configuration/App	Fixed packed bed based on solid-solid PCM			
Power	Efficiency	TES Capacity	Service Life	
A+B	A+B+C	C+D	D+E	

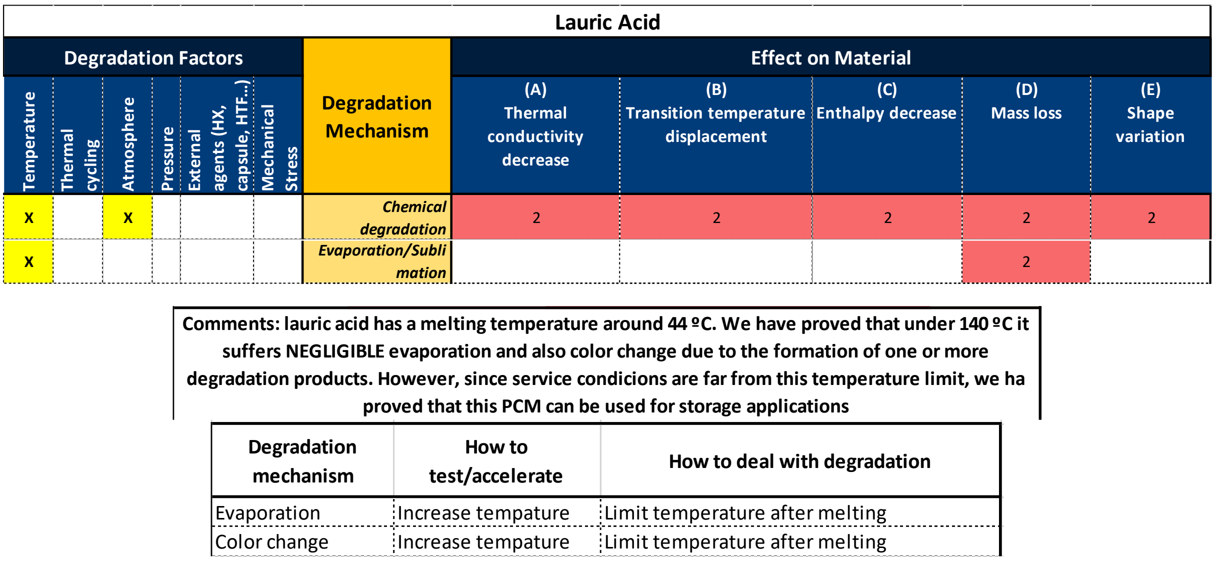
Comments: Plastic Crystals sublimate in their high temperature phase ("plastic phase"), therefore, they are affected by temperatures above their solid transition temperature.

These materials can uptake humidity from the environment. For the same reason, OPCs are not compatible with water (HTF).

Degradation mechanism	How to test/accelerate	How to deal with degradation
Sublimation	Isothermal Thermogravimetric Study (min/hour)	Confinement
Water uptake	STA under controlled atmosphere (min/hour)	Controlled environment. Use of coatings

Figure 3.3-1: Degradation mapping of organic plastic crystals (by Ángel Serrano, CIC energiGUNE)

3.3.2 Lauric acid (PCM)



Lauric Acid

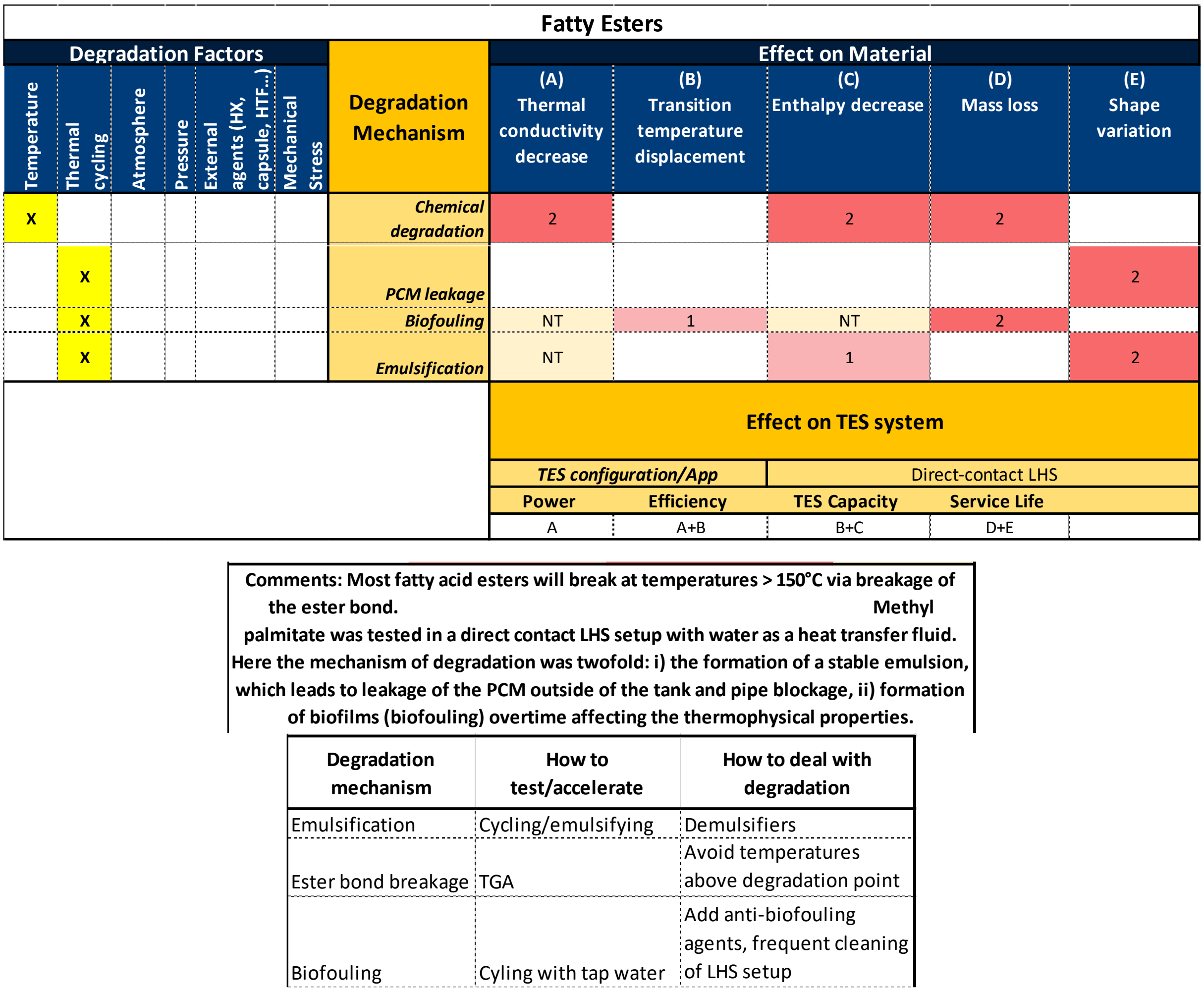
Degradation Factors						Degradation Mechanism	Effect on Material				
Temperature	Thermal cycling	Atmosphere	Pressure	External agents (HX, capsule, HTF...)	Mechanical Stress		(A) Thermal conductivity decrease	(B) Transition temperature displacement	(C) Enthalpy decrease	(D) Mass loss	(E) Shape variation
X		X				*Chemical degradation*	2	2	2	2	2
X						*Evaporation/Sublimation*				2	

Comments: lauric acid has a melting temperature around 44 ºC. We have proved that under 140 ºC it suffers NEGLIGIBLE evaporation and also color change due to the formation of one or more degradation products. However, since service condicions are far from this temperature limit, we ha proved that this PCM can be used for storage applications

Degradation mechanism	How to test/accelerate	How to deal with degradation
Evaporation	Increase tempature	Limit temperature after melting
Color change	Increase tempature	Limit temperature after melting

Figure 3.3-2: Degradation mapping of lauric acid (by Rocio Bayón, CIEMAT)

3.3.3 Fatty esters (PCM)



Fatty Esters

Degradation Factors						Degradation Mechanism	Effect on Material				
Temperature	**Thermal cycling**	**Atmosphere**	**Pressure**	**External agents (HX, capsule, HTF...)**	**Mechanical Stress**		**(A) Thermal conductivity decrease**	**(B) Transition temperature displacement**	**(C) Enthalpy decrease**	**(D) Mass loss**	**(E) Shape variation**
X						***Chemical degradation***	2		2	2	
	X					***PCM leakage***					2
	X					***Biofouling***	NT	1	NT	2	
	X					***Emulsification***	NT		1		2

Effect on TES system

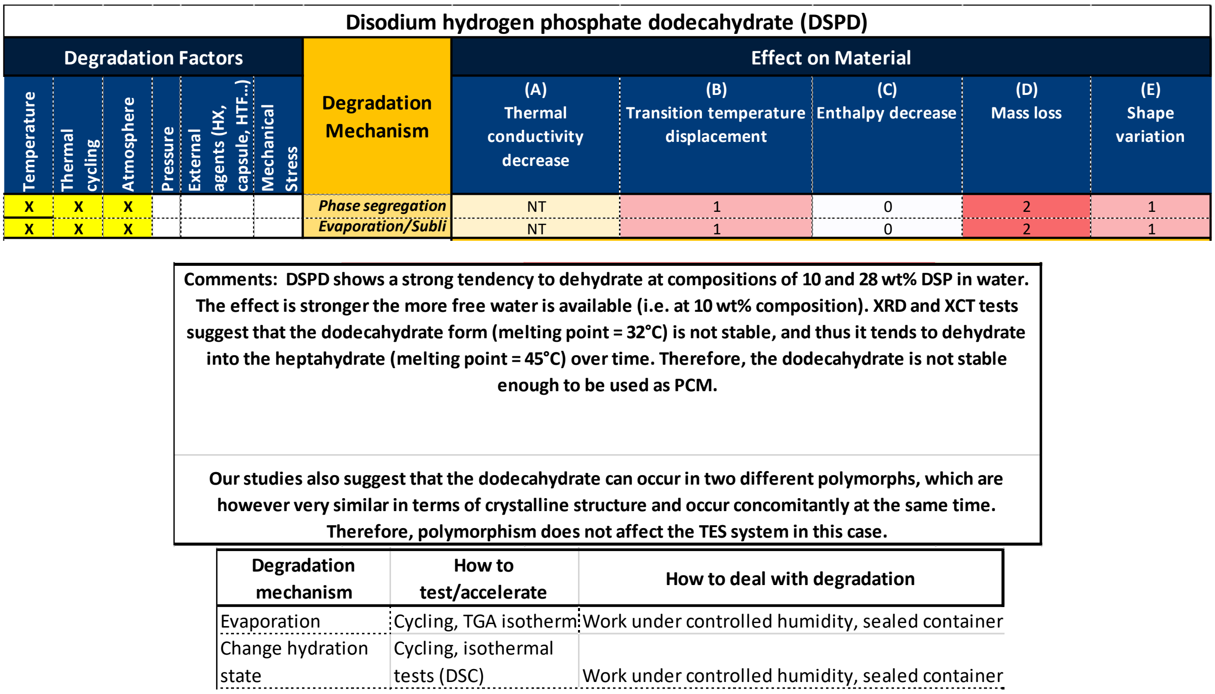
TES configuration/App	Direct-contact LHS			
Power	**Efficiency**	**TES Capacity**	**Service Life**	
A	A+B	B+C	D+E	

Comments: Most fatty acid esters will break at temperatures > 150°C via breakage of the ester bond. Methyl palmitate was tested in a direct contact LHS setup with water as a heat transfer fluid. Here the mechanism of degradation was twofold: i) the formation of a stable emulsion, which leads to leakage of the PCM outside of the tank and pipe blockage, ii) formation of biofilms (biofouling) overtime affecting the thermophysical properties.

Degradation mechanism	How to test/accelerate	How to deal with degradation
Emulsification	Cycling/emulsifying	Demulsifiers
Ester bond breakage	TGA	Avoid temperatures above degradation point
Biofouling	Cyling with tap water	Add anti-biofouling agents, frequent cleaning of LHS setup

Figure 3.3-3: Degradation mapping of fatty esters (by Rebecca Ravotti, HSLU)

3.3.4 Disodium hydrogen phosphate dodecahydrate (PCM)



Disodium hydrogen phosphate dodecahydrate (DSPD)

Degradation Factors						Degradation Mechanism	Effect on Material				
Temperature	Thermal cycling	Atmosphere	Pressure	External agents (HX, capsule, HTF...)	Mechanical Stress		(A) Thermal conductivity decrease	(B) Transition temperature displacement	(C) Enthalpy decrease	(D) Mass loss	(E) Shape variation
X	X	X				*Phase segregation*	NT	1	0	2	1
X	X	X				*Evaporation/Subli*	NT	1	0	2	1

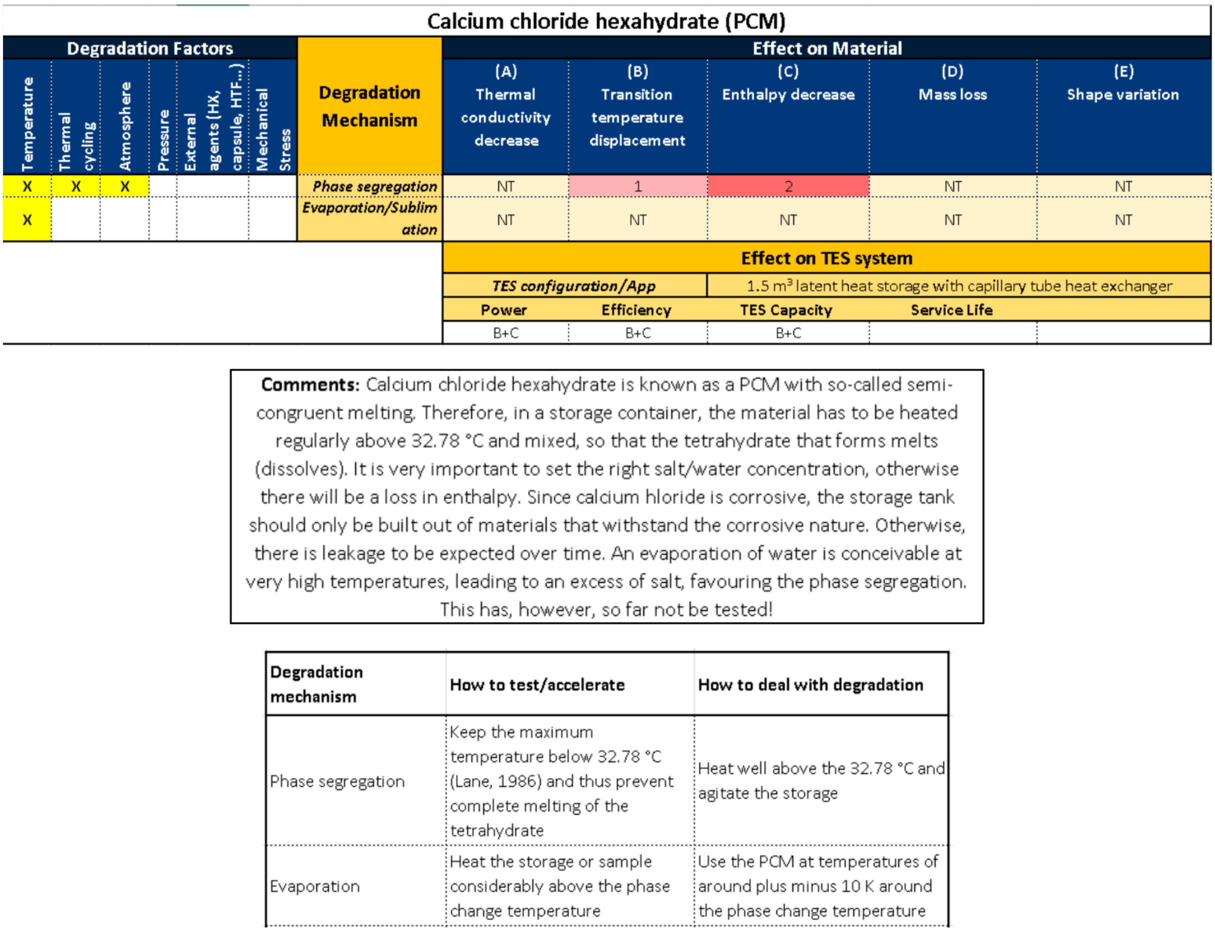
Comments: DSPD shows a strong tendency to dehydrate at compositions of 10 and 28 wt% DSP in water. The effect is stronger the more free water is available (i.e. at 10 wt% composition). XRD and XCT tests suggest that the dodecahydrate form (melting point = 32°C) is not stable, and thus it tends to dehydrate into the heptahydrate (melting point = 45°C) over time. Therefore, the dodecahydrate is not stable enough to be used as PCM.

Our studies also suggest that the dodecahydrate can occur in two different polymorphs, which are however very similar in terms of crystalline structure and occur concomitantly at the same time. Therefore, polymorphism does not affect the TES system in this case.

Degradation mechanism	How to test/accelerate	How to deal with degradation
Evaporation	Cycling, TGA isotherm	Work under controlled humidity, sealed container
Change hydration state	Cycling, isothermal tests (DSC)	Work under controlled humidity, sealed container

Figure 3.3-4: Degradation mapping of disodium hydrogen phosphate dodecahydrate (by Rebecca Ravotti, HSLU)

3.3.5 Calcium chloride hexahydrate (PCM)



Calcium chloride hexahydrate (PCM)

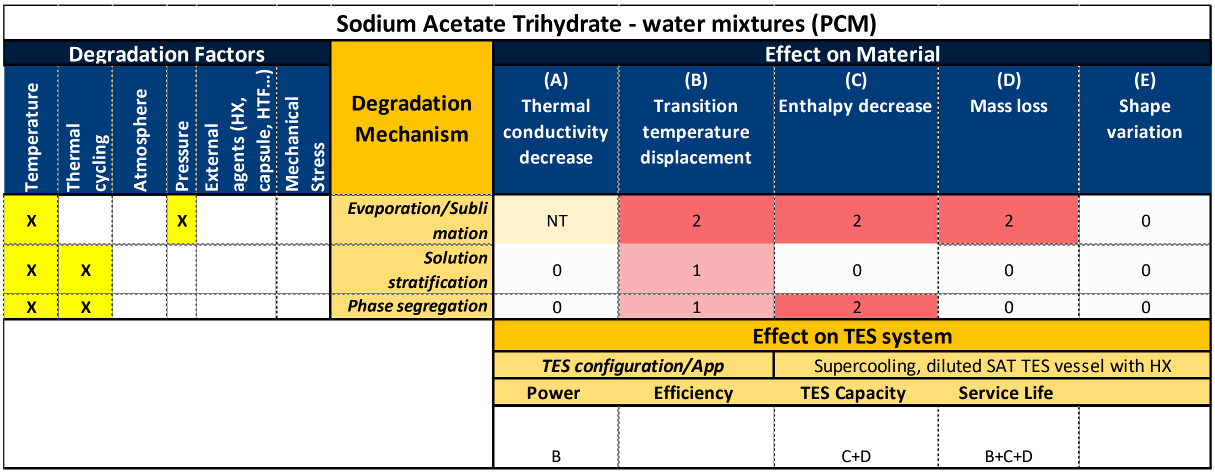
Degradation Factors						Degradation Mechanism	Effect on Material				
Temperature	Thermal cycling	Atmosphere	Pressure	External agents (HX, capsule, HTF...)	Mechanical Stress		(A) Thermal conductivity decrease	(B) Transition temperature displacement	(C) Enthalpy decrease	(D) Mass loss	(E) Shape variation
X	X	X				*Phase segregation*	NT	1	2	NT	NT
X						*Evaporation/Sublimation*	NT	NT	NT	NT	NT
							Effect on TES system				
							TES configuration/App		1.5 m³ latent heat storage with capillary tube heat exchanger		
							Power	Efficiency	TES Capacity	Service Life	
							B+C	B+C	B+C		

Comments: Calcium chloride hexahydrate is known as a PCM with so-called semi-congruent melting. Therefore, in a storage container, the material has to be heated regularly above 32.78 °C and mixed, so that the tetrahydrate that forms melts (dissolves). It is very important to set the right salt/water concentration, otherwise there will be a loss in enthalpy. Since calcium hloride is corrosive, the storage tank should only be built out of materials that withstand the corrosive nature. Otherwise, there is leakage to be expected over time. An evaporation of water is conceivable at very high temperatures, leading to an excess of salt, favouring the phase segregation. This has, however, so far not be tested!

Degradation mechanism	How to test/accelerate	How to deal with degradation
Phase segregation	Keep the maximum temperature below 32.78 °C (Lane, 1986) and thus prevent complete melting of the tetrahydrate	Heat well above the 32.78 °C and agitate the storage
Evaporation	Heat the storage or sample considerably above the phase change temperature	Use the PCM at temperatures of around plus minus 10 K around the phase change temperature

Figure 3.3-5: Degradation mapping of calcium chloride hexahydrate (by Henri Schmit, ZAE Bayern)

3.3.6 Sodium acetate trihydrate – water mixtures (PCM)



Sodium Acetate Trihydrate - water mixtures (PCM)

Degradation Factors						Degradation Mechanism	Effect on Material				
Temperature	Thermal cycling	Atmosphere	Pressure	External agents (HX, capsule, HTF...)	Mechanical Stress		(A) Thermal conductivity decrease	(B) Transition temperature displacement	(C) Enthalpy decrease	(D) Mass loss	(E) Shape variation
X			X			*Evaporation/Sublimation*	NT	2	2	2	0
X	X					*Solution stratification*	0	1	0	0	0
X	X					*Phase segregation*	0	1	2	0	0

Effect on TES system

TES configuration/App	Supercooling, diluted SAT TES vessel with HX			
Power	**Efficiency**	**TES Capacity**	**Service Life**	
B		C+D	B+C+D	

Comments:

1- Sodium acetate trihydrate (SAT) - water as well as other salt hydrate compounds suffer most greatly from improper management of water vapour loss as this will permanently alter the mixture composition and, thus, its binary equilibrium phase change characteristics. Due to the high molar ratio of water to anhydrous salt, saturated water vapour pressure above the solutions remains high and is therefore liable to vapour loss at temperatures > 60 degC if not properly managed.

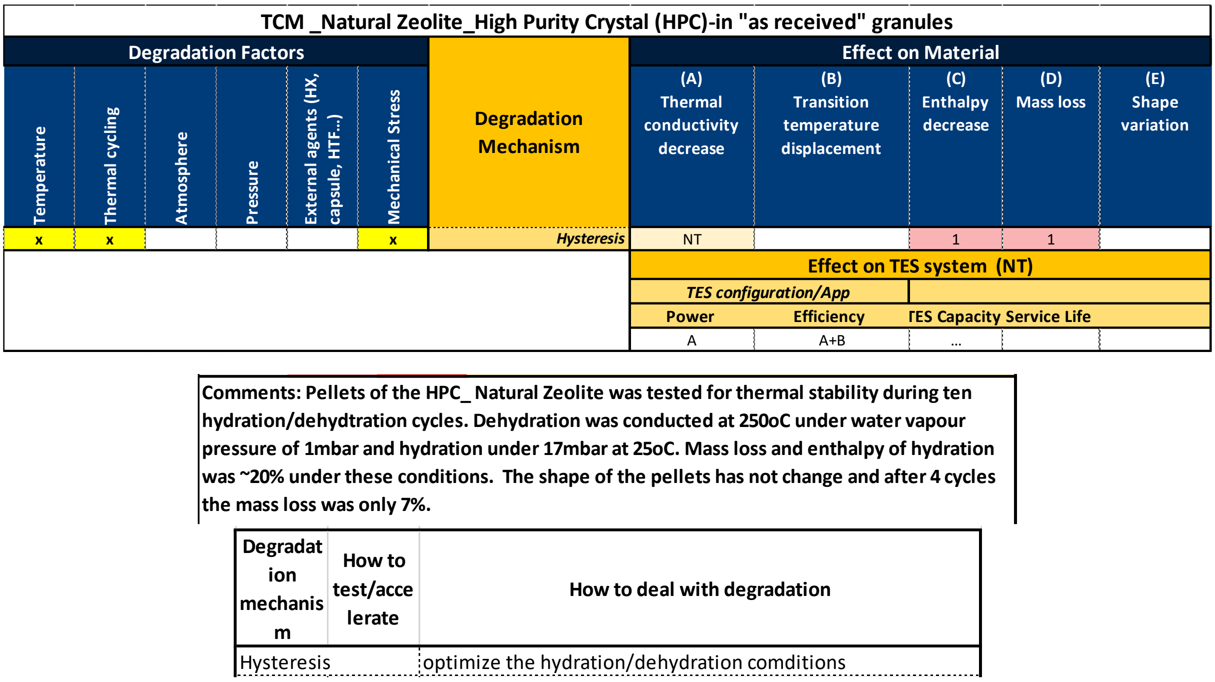
2- When using salt hydrate-water mixtures without thickeners, a vertical concentration gradient will innevitably arise, but will stabilize with time, not affecting the total available enthalpy, but redistributing it to the zones of higher salt concentration. Height of the vessel and the intensity of the heat flux giving rise to internal convection will each impact the concentration distribution over long term operation of the TES. Note that a more dilute salt hydrate-water mixture will result in more severe solution stratification, so may not be suitable for use in tall vessels as the available area for heat transfer during phase change will be limited only to the bottom of the vessel as well as significantly alter the local solubility/Tsat of the salt solution. More concentrated mixtures are overall more resistant to these shifts in Tsat.

3 - Phase segregation, i.e., formation of anhydrous salt, for incongruent salt systems can be avoided with sufficiently elevated and lengthy heat soak during the charge phase to ensure complete dissolution of the salt and allow for potentially slow dynamics of this dissolution (mass diffusion at the interface of anhydrous salt-aqueous solution)

Degradation mechanism	How to deal with degradation
evaporation (loss of water vapour)	Closed vessel with or without expansion tank maintained at > 0 atm_g. When using an external expansion tank, ensure that tube/hose run and expansion tank connection are arranged/oriented to permit reflux of condensed water vapour to the PCM vessel. Extra water, even in very minute quantities, is recommended to ensure slightly greater than the stoichiometric ratio of water to SA needed to form the desired hydrate compound. Also, vented vessels are prone to inducing heterogeneous nucleation in salt hydrate solutions that are intended to supercool due to both dehydration of salt at the liquid-vapour interface, but also from particulate contaminant transfer from ambient air
Solution stratification	Increased heat transfer intensity during charging phase may improve mixing and shift concentrated salt stratum towards the top of the vessel, but a stable concentration gradient in the liquid phase will develop over the long term but this should not decrease available enthalpy if there is no anhydride formation nor loss of water vapour. Available enthalpy becomes redistributed to the more concentrated strata, affecting mainly the heat transfer by way of affecting the temperature field along the height of the HX during phase change processes, favouring lower portions over higher ones. Select vessel height appropriately for the salt hydrate-water average concentration and typical heat flux. Increased height will both aide internal convection, but also intensify stratification, therefore not alone a means of improving solution mixing. If heat flux is insufficent, it is advised to reduce vessel height and increase width-depth instead.
Phase segregation	Superheating treatment is necessary to ensure complete dissolution of SA-water mixture on every cycle where solidification of SAT occurs (with or without supercooling/triggered nucleation).

Figure 3.3-6: Degradation mapping of SAT-water mixtures (by Louis Desgrosseilliers, SPF)

3.3.7 Zeolite (TCM)



TCM _Natural Zeolite_High Purity Crystal (HPC)-in "as received" granules

Degradation Factors						Degradation Mechanism	Effect on Material				
Temperature	Thermal cycling	Atmosphere	Pressure	External agents (HX, capsule, HTF...)	Mechanical Stress		(A) Thermal conductivity decrease	(B) Transition temperature displacement	(C) Enthalpy decrease	(D) Mass loss	(E) Shape variation
x	x				x	*Hysteresis*	NT		1	1	

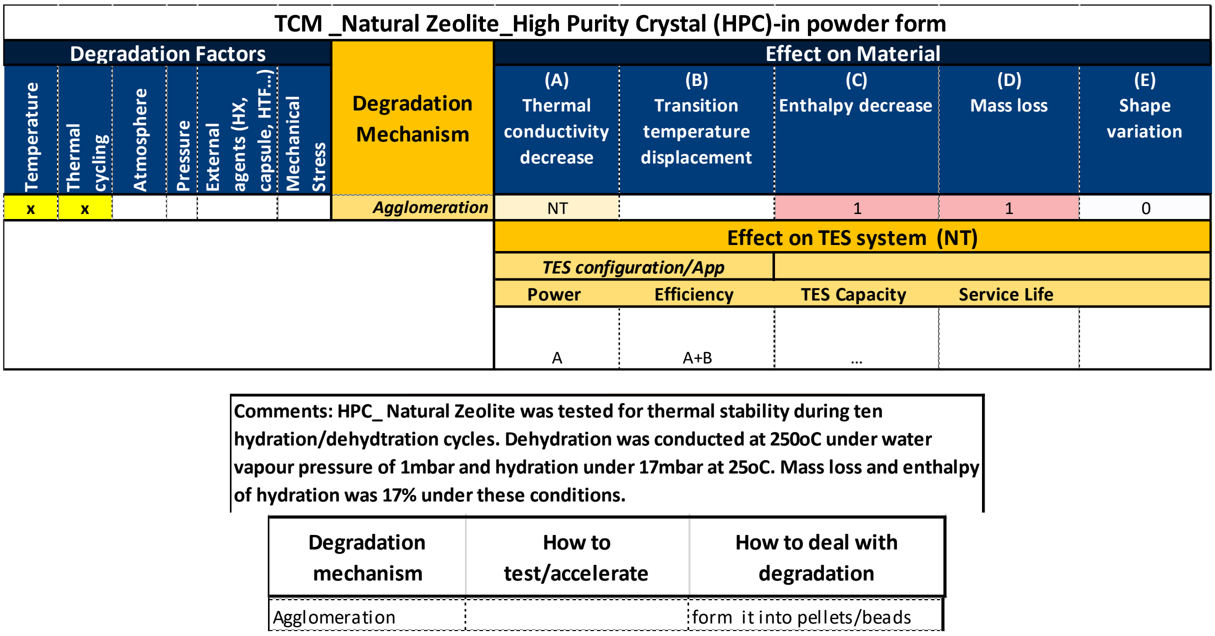
Effect on TES system (NT)

TES configuration/App			
Power	Efficiency	TES Capacity	Service Life
A	A+B	...	

Comments: Pellets of the HPC_ Natural Zeolite was tested for thermal stability during ten hydration/dehydtration cycles. Dehydration was conducted at 250oC under water vapour pressure of 1mbar and hydration under 17mbar at 25oC. Mass loss and enthalpy of hydration was ~20% under these conditions. The shape of the pellets has not change and after 4 cycles the mass loss was only 7%.

Degradation mechanism	How to test/accelerate	How to deal with degradation
Hysteresis		optimize the hydration/dehydration comditions

Figure 3.3-7: Degradation mapping of zeolite pellets (by Lia Kouchachvili, CanmetENERGY)



TCM _Natural Zeolite_High Purity Crystal (HPC)-in powder form

Degradation Factors						Degradation Mechanism	Effect on Material				
Temperature	Thermal cycling	Atmosphere	Pressure	External agents (HX, capsule, HTF...)	Mechanical Stress		(A) Thermal conductivity decrease	(B) Transition temperature displacement	(C) Enthalpy decrease	(D) Mass loss	(E) Shape variation
x	x					*Agglomeration*	NT		1	1	0

Effect on TES system (NT)

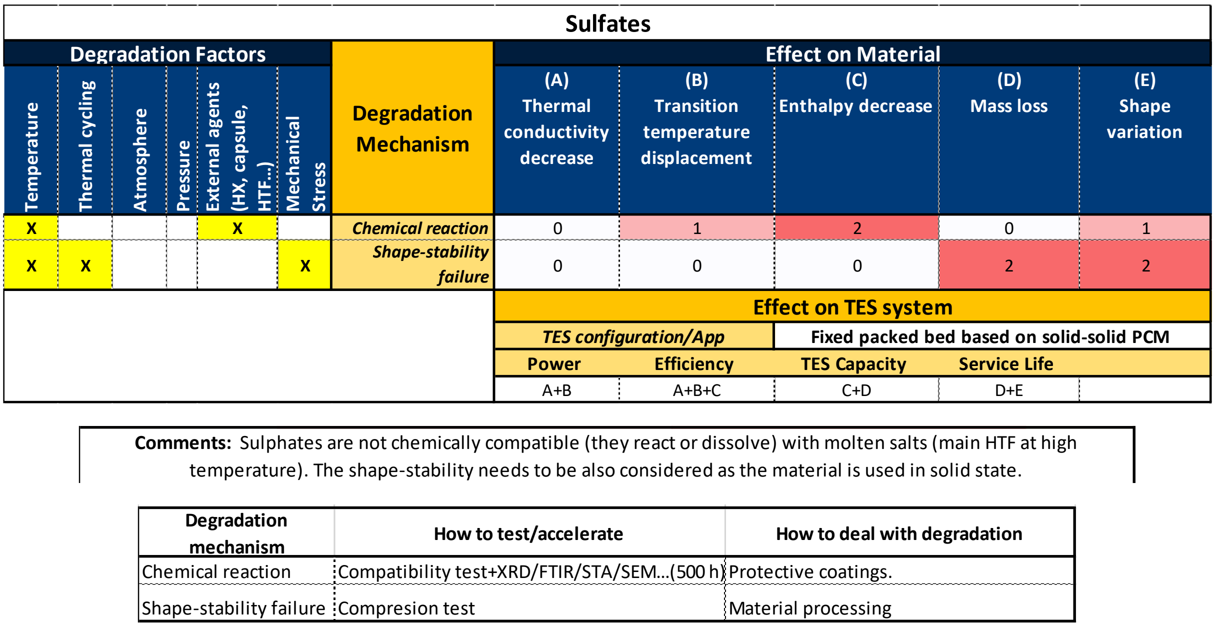
TES configuration/App			
Power	Efficiency	TES Capacity	Service Life
A	A+B	...	

Comments: HPC_ Natural Zeolite was tested for thermal stability during ten hydration/dehydtration cycles. Dehydration was conducted at 250oC under water vapour pressure of 1mbar and hydration under 17mbar at 25oC. Mass loss and enthalpy of hydration was 17% under these conditions.

Degradation mechanism	How to test/accelerate	How to deal with degradation
Agglomeration		form it into pellets/beads

Figure 3.3-8: Degradation mapping of zeolite powder (by Lia Kouchachvili, CanmetENERGY)

3.3.8 Sulfates (TCM)



Sulfates											
Degradation Factors						**Degradation Mechanism**	**Effect on Material**				
Temperature	**Thermal cycling**	**Atmosphere**	**Pressure**	**External agents (HX, capsule, HTF...)**	**Mechanical Stress**		**(A) Thermal conductivity decrease**	**(B) Transition temperature displacement**	**(C) Enthalpy decrease**	**(D) Mass loss**	**(E) Shape variation**
X				X		*Chemical reaction*	0	1	2	0	1
X	X				X	*Shape-stability failure*	0	0	0	2	2

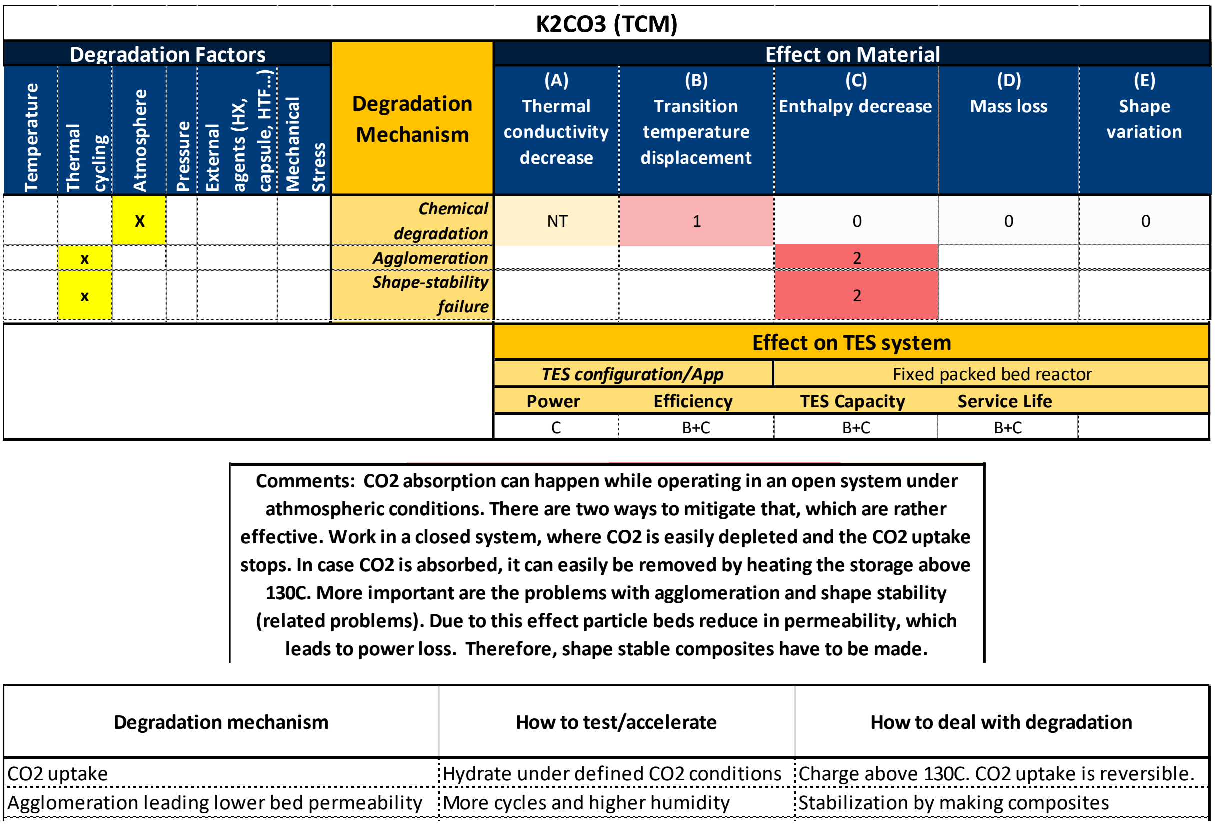
Effect on TES system			
TES configuration/App	Fixed packed bed based on solid-solid PCM		
Power	Efficiency	TES Capacity	Service Life
A+B	A+B+C	C+D	D+E

Comments: Sulphates are not chemically compatible (they react or dissolve) with molten salts (main HTF at high temperature). The shape-stability needs to be also considered as the material is used in solid state.

Degradation mechanism	How to test/accelerate	How to deal with degradation
Chemical reaction	Compatibility test+XRD/FTIR/STA/SEM...(500 h)	Protective coatings.
Shape-stability failure	Compresion test	Material processing

Figure 3.3-9: Degradation mapping of sulfates (by Ángel Serrano, CIC energiGUNE)

3.3.9 Potassium carbonate (TCM)



K2CO3 (TCM)											
Degradation Factors						**Degradation Mechanism**	**Effect on Material**				
Temperature	**Thermal cycling**	**Atmosphere**	**Pressure**	**External agents (HX, capsule, HTF...)**	**Mechanical Stress**		**(A) Thermal conductivity decrease**	**(B) Transition temperature displacement**	**(C) Enthalpy decrease**	**(D) Mass loss**	**(E) Shape variation**
		X				*Chemical degradation*	NT	1	0	0	0
	x					*Agglomeration*			2		
	x					*Shape-stability failure*			2		

Effect on TES system			
TES configuration/App	Fixed packed bed reactor		
Power	Efficiency	TES Capacity	Service Life
C	B+C	B+C	B+C

Comments: CO2 absorption can happen while operating in an open system under athmospheric conditions. There are two ways to mitigate that, which are rather effective. Work in a closed system, where CO2 is easily depleted and the CO2 uptake stops. In case CO2 is absorbed, it can easily be removed by heating the storage above 130C. More important are the problems with agglomeration and shape stability (related problems). Due to this effect particle beds reduce in permeability, which leads to power loss. Therefore, shape stable composites have to be made.

Degradation mechanism	How to test/accelerate	How to deal with degradation
CO2 uptake	Hydrate under defined CO2 conditions	Charge above 130C. CO2 uptake is reversible.
Agglomeration leading lower bed permeability	More cycles and higher humidity	Stabilization by making composites

Figure 3.3-10: Degradation mapping of potassium carbonate (by Henk Huinink, TU Eindhoven)

3.4 Conclusions

The developed approach to map degradation of CTES materials provides a comprehensive overview of the degradation mechanisms and the corresponding degradation factors which are relevant for a specific material or material class. Such a mapping diagram informs about the effect of different types of degradation on the CTES material and system.

It becomes evident that a certain effect on the material (e.g. a transition temperature displacement) can be caused by different degradation mechanisms (cf. example of SAT-water mixtures in section 3.3.6). In the same way, effects on the storage system behaviour can usually be attributed to a combination of different effects on the material. In practice, this means that stability tests under application conditions can only be carried out reasonably if there is already an understanding of the dependencies between degradation factors, degradation mechanisms and effects on the CTES material and system. Such an understanding can be summarized and communicated using the developed degradation mapping diagram.

4 Literature

[1] W. van Helden, A. Hauer et al. (2020). Material and Component Development for Thermal Energy Storage, *IEA SHC Task 58 / ES Annex 33 Final Report*, available at https://iea-es.org/publications/final-report-annex-33/

[2] J. G. C. Storch (2010). Materialwissenschaftliche Untersuchungen an zeolithischen Adsorbenzien für den Einsatz in offenen Sorptionssystemen zur Wärmespeicherung, Doctoral dissertation, *Technical University Munich*, available at https://mediatum.ub.tum.de/doc/820976/820976.pdf

[3] Rathgeber, C., Hiebler, S., Bayón, R., Cabeza, L. F., Zsembinszki, et al. (2020). Experimental devices to investigate the long-term stability of phase change materials under application conditions. *Applied Sciences*, 10(22), 7968.

[4] Ferrer, G., Solé, A., Barreneche, C., Martorell, I., and Cabeza, L. F. (2015). Review on the methodology used in thermal stability characterization of phase change materials. *Renewable and Sustainable Energy Reviews*, 50, 665-685.

[5] Bayón, R. and Rojas, E. (2019). Development of a new methodology for validating thermal storage media: Application to phase change materials. *International Journal of Energy Research*, 43(12), 6521-6541.

[6] Mehling, H. (2023). Review and Analysis of Existing Approaches to Investigate Property Degradation of Phase Change Materials and Development of a New Systematic Approach. *Applied Sciences*, 13(15), 8682.