SOLAR HEATING & COOLING PROGRAMME
INTERNATIONAL ENERGY AGENCY

How to determine and categorise materials performance degradation?

Dr. Christoph Rathgeber
IEA SHC Solar Academy Webinar, 1 April 2025

How to determine and categorise materials performance degradation?

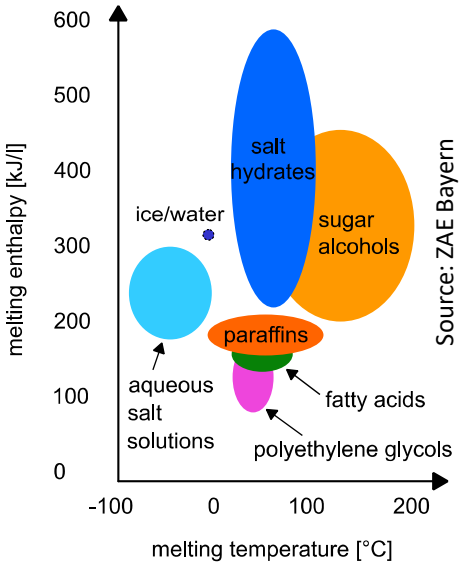
- What affects the stability of PCM and TCM?
- What is reported in scientific literature, what is missing?

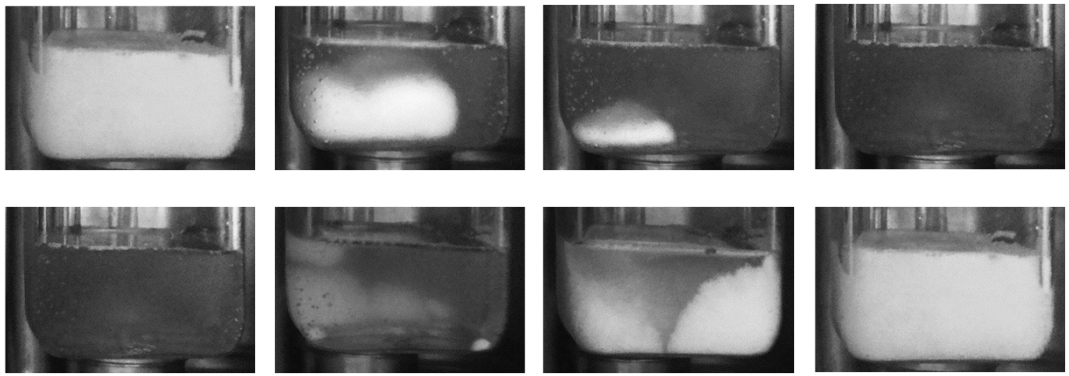
- Investigating degradation under application conditions
- Mapping degradation

- Summary and conclusions
- References

What affects the stability of PCM?

- Different material classes are used as PCM.
- In applications, PCM are thermally cycled.





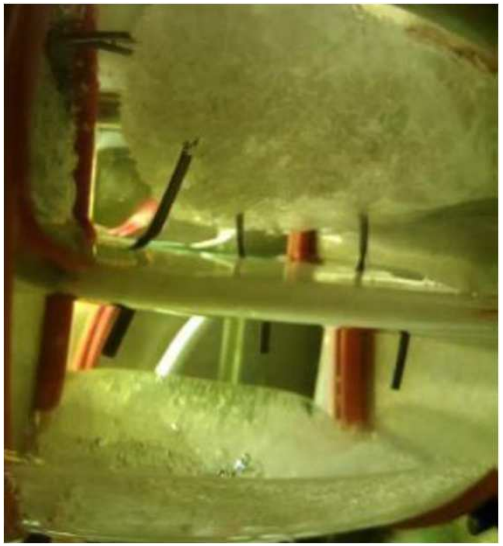
Source: ZAE Bayern

Degradation of PCM – Examples

- Chemical degradation at high temperatures (organic materials)
- Phase separation (salt hydrates and mixtures)

Source: [1]

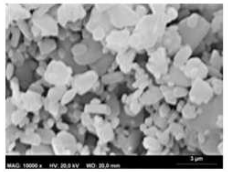
D-mannitol after 166 h melted under air @180 ºC



Source: ZAE Bayern

What affects the stability of TCM?

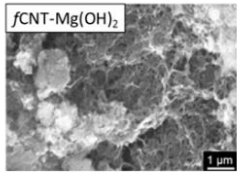
- Different material classes and composites are used as TCM.
- In applications, TCM are subject to heat and mass transfer processes.



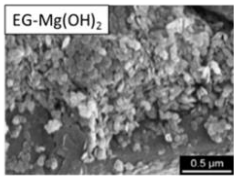
$CaC_2O_4 \cdot H_2O$
Institute of Applied Synthetic Chemistry (TU Wien)
Dr. Peter Weinberger

$Vermiculite\text{-}CaCl_2$

Swansea University
Dr. Jonathon Elvis



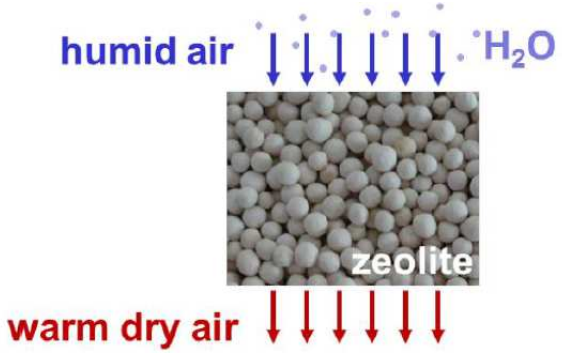
Carbon nanotube-$Mg(OH)_2$



Expanded graphite-$Mg(OH)_2$

University of Messina – Engineering Department

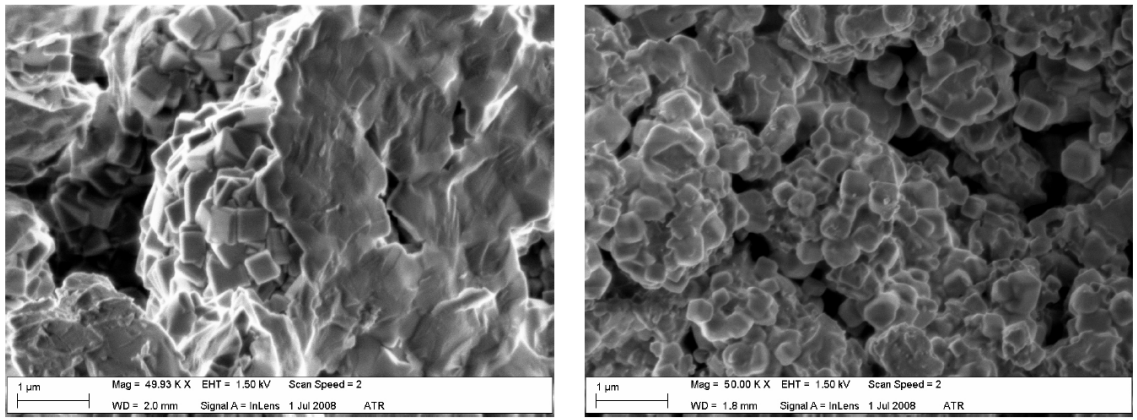
Prof. dr. Candida Milone



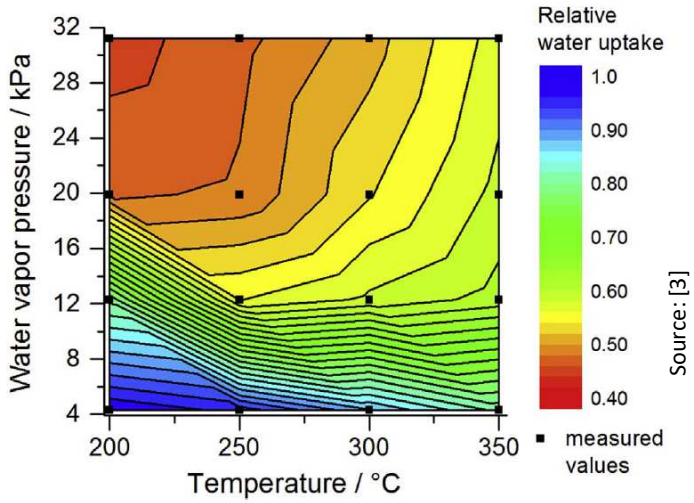
Source: [1]

Degradation of TCM – Examples

- Breaking up of pellets or composites by hydrothermal aging
- Transformation of crystalline materials into amorphous phases



Source: [2]



Source: [3]

What is reported in scientific literature?

- Review paper on tested materials and applied methods [4]
- Method to validate storage materials [5]
- Systematic approach to investigate property degradation [6]

Review on the methodology used in therma
of phase change materials

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Thermal energy storage (TES)

ABSTRACT

In general, PCM are classified in orgar
fatty acids, and sugar alcohols. Inorg
Eutectics and mixtures are also being
important PCM requirements is being
as cycling stability. A PCM should prese
after a repeated number of freezing
procedures are classified by PCM type
to perform cycling stability tests are h
issues: the choice of the equipment to
the PCM before and after thermal cycl
number of cycles to perform; and final
dynamic, or others) to perform the te
common standard for thermal cycling

SPECIAL ISSUE RESEARCH ARTICLE

Development of a new methodolog
storage media: Application to phas

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Summary
Long-term stability and long-te
key issue that should be thorou
However, no testing protocol
age media, so that authors app
ing procedures but also for pre
operation. This paper aims to
validating thermal storage
(PCMs). This methodology co
acterization, preliminary asse
designing the accelerated life
obtained in order to predict PC
from shorter tests performed u
this methodology will be valid
chemical storage media, too.

KEYWORDS
lifetime relationship models, long-term
media, validation methodology

applied sciences

MDPI

Article

Review and Analysis of Existing Approaches to Investigate Property Degradation of Phase Change Materials and Development of a New Systematic Approach

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Abstract: With increasing commercial success of PCM, the long-term development of properties becomes more important. It has been investigated already for decades in a variety of ways and a wide range of testing conditions. Previous reviews concluded that further work toward standardization of testing is needed. In a desktop study, the current approach to testing was analyzed. It is shown that standardization should not mean to always test with the same methods using the same conditions, e.g., as different applications impose different conditions. Instead, testing should be tailored to the individual case. For this, a new, systematic approach was developed. It identifies first the basic functions and related properties that might be subject to testing, e.g., with a specific application in mind, and then gives an approach to find the degradation effects and underlying mechanisms to allow tailoring and optimizing test procedures. As an example, the approach is applied to the function of heat storage. Here, a new degradation effect was identified, and for degradation by phase separation, it is shown by an example that it could even be reversed at suitable conditions. Therefore, tailoring testing conditions to the individual case is needed. Deeper knowledge of degradation mechanisms is required, so further R&D is suggested.

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Bayón and Rojas 2019 [5]

- Bayón and Rojas propose a method to validate TES materials.
- “No testing protocol or guideline exists […] 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.”
- To perform accelerated tests, it is crucial to know the relevant degradation factors (e.g. high-temperature, oxygen atmosphere, etc.) and to perform “tests under increasing stress level of degradation factors”.

Mehling 2023 [6]

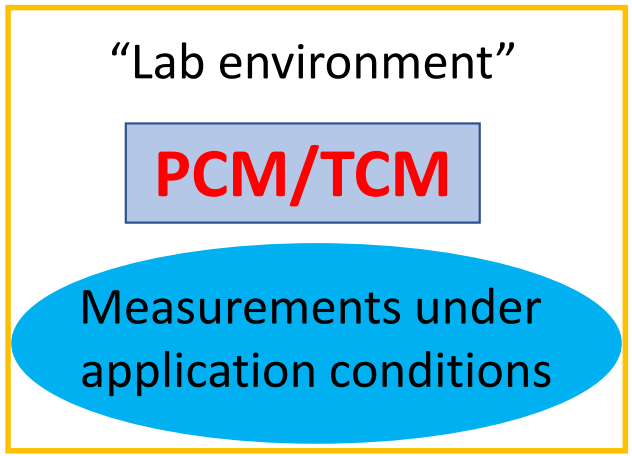
- Mehling presents an approach to investigate property degradation of PCM.
- “As different applications impose different conditions […], testing should be tailored to the individual case”.
- First step: Identify “the basic functions and related properties that might be subject to testing, e.g., with a specific application in mind.”

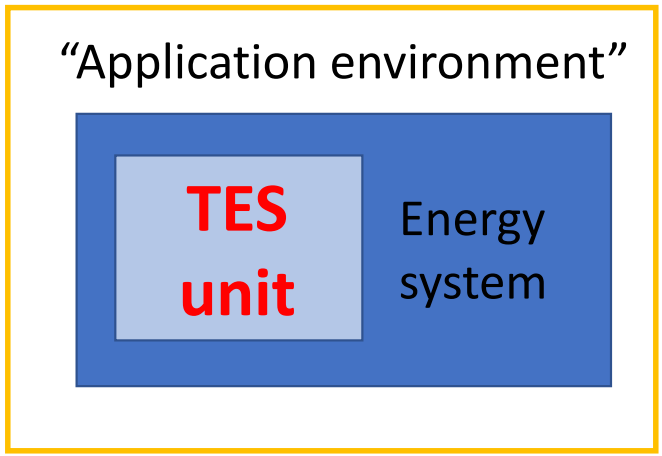
What is missing in scientific literature?

Material (class)-specific information on:

- Classification and differentiation of relevant degradation mechanisms
- Suitable test methods to investigate degradation under application conditions
- Recommended procedures to accelerate degradation in order to speed up degradation tests

Investigating degradation under application conditions





Investigating degradation under application conditions

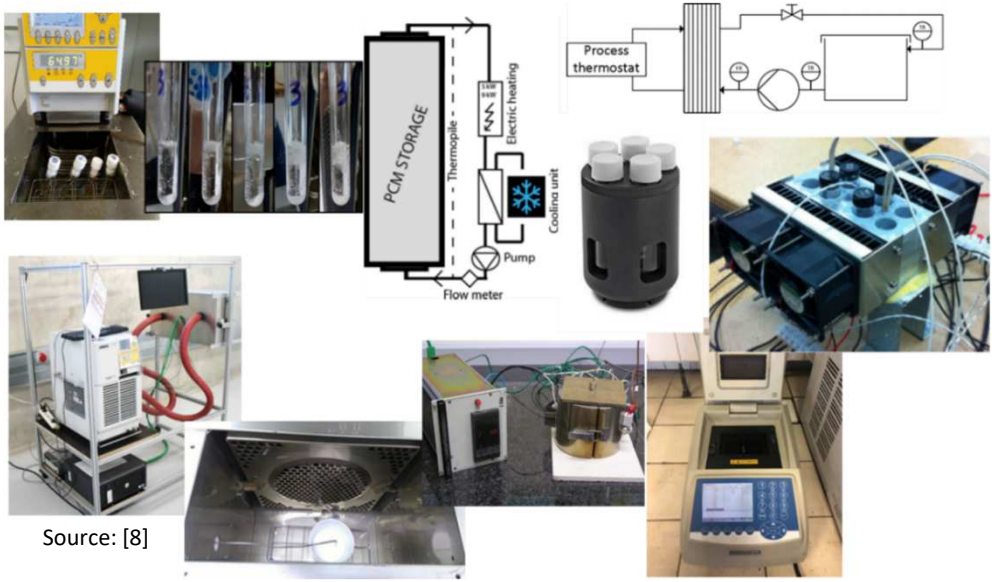
applied sciences

MDPI

Article

Experimental Devices to Investigate the Long-Term Stability of Phase Change Materials under Application Conditions

Christoph Rathgeber [1,*], Stefan Hiebler [1], Rocío Bayón [2], Luisa F. Cabeza [3], Gabriel Zsembinszki [3], Gerald Englmair [4], Mark Dannemand [4], Gonzalo Diarce [5], Oliver Fellmann [6], Rebecca Ravotti [6], Dominic Groulx [7], Ali C. Kheirabadi [7], Stefan Gschwander [8], Stephan Höhlein [9], Andreas König-Haagen [9], Noé Beaupere [10,11] and Laurent Zalewski [10]



Source: [8]

Mapping degradation

- Provide an overview of the relationships between
  - test conditions,
  - degradation mechanisms,
  - effects on the material,
  - effects on the CTES system
- …and give recommendations for accelerated degradation testing.

Mapping degradation

- Guiding questions:
  - What are the reasons for degradation?
  - What are the effects of degradation on the material properties?
  - How to identify and quantify degradation?
  - How to accelerate degradation to achieve fast testing?
- Degradation mapping approaches were proposed, discussed, and further refined in Task 67.

Mapping degradation – first approach

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

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

Stability …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

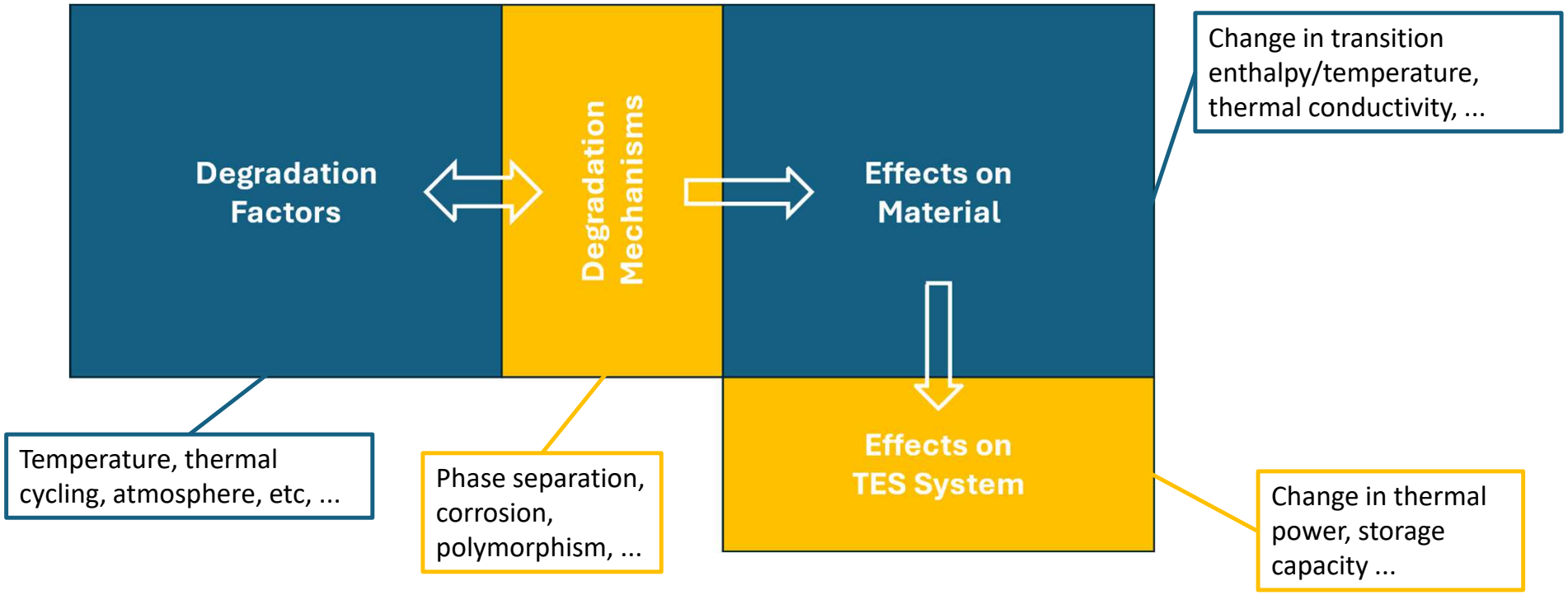
→ HPLC, GM-Chromatography, FTIR spectroscopy, Changes in ΔH_{fus} (DSC), in TGA curve, in color (Vis-UV spectróscopy), etc

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

Content by: CIEMAT; corresponding article: [7]

Mapping degradation – second approach



Mapping degradation – 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	

Content by: Lucerne University of Applied Sciences and Arts

1: moderate
2: very high
NT: not tested

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

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.

Mapping degradation – K_2CO_3 (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	

Content by: TU Eindhoven

0: negligible
1: moderate
2: very high
NT: not tested

Degradation mechanism	How to test/accelerate
CO2 uptake	Hydrate under defined CO2 conditions
Agglomeration leading lower bed permeability	More cycles and higher humidity

How to deal with degradation
Charge above 130C. CO2 uptake is reversible.
Stabilization by making composites

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.

Summary and conclusions

- A PCM/TCM is stable if its properties remain within a certain limit.
  - Properties: Melting/reaction enthalpy, chemical composition, transition temperature etc.
- CTES material stability depends on
  - the nature of the material (class)
  - the operating conditions of the application or laboratory test.
- Statements of the type "*Material xy is stable.*" or "*Material xy is not stable.*" should not be made without reporting the testing conditions.

Summary and conclusions

- Understanding stability at CTES component and system level starts with degradation processes on material level.
- Stability mapping tables offer a visualization of CTES material degradation behaviour.
- Experiments to accelerate degradation were discussed to speed up stability investigations.
- In many cases, operating conditions can be selected that allow an application without performance reduction caused by material degradation!

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Thank you for your attention!

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