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Development of a new methodology for validating thermal storage media: Application to phase change materials

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Summary
Long-term stability and long-term performance of thermal storage media are a key issue that should be thoroughly analysed when developing storage systems. However, 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. This paper aims to cover this gap by proposing a methodology for validating thermal storage media; in particular, phase change materials (PCMs). This methodology consists of different stages that include PCM characterization, preliminary assessment tests, and accelerated life testing. For designing the accelerated life tests, lifetime relationship models have to be obtained in order to predict PCM long-term behaviour under service conditions from shorter tests performed under stress conditions. The approach followed in this methodology will be valid for materials to be used as sensible or thermochemical storage media, too.

KEYWORDS
lifetime relationship models, long-term performance, phase change materials, PCM, thermal storage media, validation methodology

1 | INTRODUCTION

Thermal energy storage is one of the research topics that have been attracting much attention during the last decades because of its capacity to make certain renewables dispatchable, to make waste heat useful, and to increase thermal inertia in buildings, clothes, and shoes.[1] The most critical factor in any thermal storage system is the medium in which the heat is stored. This heat can be stored by changing the temperature of the medium (sensible heat storage), by changing its phase (latent heat), or by producing a chemical reaction (thermochemical storage).

When choosing a storage material for any of these mechanisms, the first thing to take into account is the temperature value or range of the specific application, after which we have to look at the thermophysical properties that make this material suitable for thermal storage. Apart from having adequate values, it is very important that these thermophysical properties remain sufficiently constant along the whole service life of the storage system. Therefore, the long-term reliability of thermal storage media is a question of main concern. A storage medium can be interesting from the point of view of thermophysical properties but loose its charm when those properties change along the expected lifetime of the system.

Since the early 80s, many researchers have paid attention to this issue, so that literature abounds in papers reporting on feasibility studies of storage materials.[2-17] However, it is in the field of latent heat storage materials, which are usually called phase change materials (PCMs), where we can find the majority of these studies. This is due to the large number of PCMs that are suitable for applications in a very wide temperature range[18-23] (from 0°C to 800°C). Taking into account that the thermophysical properties that make PCMs suitable as storage media are phase change temperature (T_{ph-ch}) and enthalpy (ΔH_{ph-ch}), Figure 1 represents ΔH_{ph-ch} vs T_{ph-ch} for PCMs that undergo solid-liquid transitions together with the temperature ranges of the possible storage applications. As we can see, hydrated salts and organic materials (sugar alcohols, paraffins, fatty acids, etc) are the PCMs considered for low- and medium-temperature applications (less than 200°C), whereas inorganic salts and metals are the most appropriate latent storage materials for higher temperature processes. Although conventional PCMs usually undergo solid-liquid transitions, there are also materials that exchange latent heat through solid-solid[24] and liquid-liquid[25] transitions.

Despite the wide range of potential applications, the commercial implementation of latent storage systems is very often hindered by the lack of validated PCMs. Most of the studies found in literature aiming to assess the reliability of PCMs as latent storage media have focused their attention on thermal cycling. Table 1, based on a thorough review of literature from the early 80s till today, summarizes the thermal cycling tests performed by different authors for evaluating and assessing the feasibility of PCMs. This table distinguishes the kind of PCMs studied, the cycling conditions, the used set-up, and also the analytical technique(s) applied for evaluating PCM properties

after the tests. According to this review, most tested PCMs are intended for storage applications at temperatures below 100°C. Those PCMs include pure substances, eutectic mixtures, and composites that undergo either solid-liquid[26-29,31-46,48-58,65,67-69,75-77,79-82,85-87] or solid-solid[30,63,78,83,84,88,89] phase transitions. In contrast, only few stability studies have been found for PCMs intended to temperature applications[47,59-62,64,66,70-74] above 100°C.

In order to perform cycling tests, some authors used differential scanning calorimetry (DSC),[27,30,40,59,60,66-68,77,82,85,89] whereas the majority used set-ups adapted and/or designed on purpose. Those set-ups included thermostatic chambers,[26,31,33,41-44,47,54,57,63,65,70,79,83,86-88] thermal water baths,[28,29,32,34-36,46,52,56,69] electric hot plates with temperature control,[37-39,45,62] weathering chambers,[48,51,55,58,75,76,78] ovens with controlled heating,[35,49,61,64,71,72,74,80] and, in few cases, also with a cooling control.[50,53,73] The advantage of using a DSC apparatus for thermal cycling is that phase change temperature (T_{ph-ch}) and calculated enthalpy (ΔH_{ph-ch}) are recorded directly for each cycle, so that their evolution can be monitored without interrupting the test or removing the sample. If a DSC apparatus is not used to perform the cycling tests, these thermophysical properties have to be measured after a certain number of cycles mainly by DSC or thermogravimetric analysis (TGA). Additionally, for detecting chemical or structural changes in the PCMs after the cycling, some authors applied analytical techniques like, for example, Fourier transform infrared spectroscopy (FTIR),[46,48,51,57,59,61,63,65,69,75,78,83,88] visible and ultraviolet spectroscopy (VisUV),[64] X-ray diffraction (XRD),[60,74] high performance liquid chromatography (HPLC),[61] or scanning electron microscopy (SEM).[57,60,74,75,77,80]
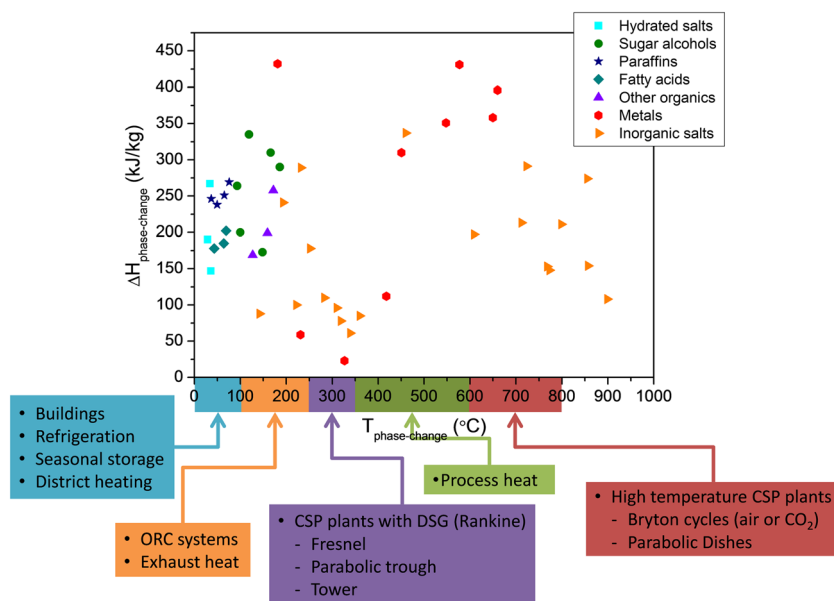
FIGURE 1 ΔH_{ph-ch} vs T_{ph-ch} for potential PCMs. The temperature ranges required by different thermal storage application have been indicated as well [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Overview of the thermal cycling tests performed by different authors for assessing PCM reliability in chronological order from early 80s up to today.

Year-Author Reference	Institution (Country)	PCM T_{ph-ch}	Thermal Cycling Characteristics			Accelerated Test?
			Experimental Set-up	No. of Cycles (T interval)	PCM Evaluation	
1980-Marks S[26]	U. Delaware (USA)	Glaubert salt (Na$_2$SO$_4$.10H$_2$O) 32°C	Thermal cycling chamber	1130 (11-41°C)	ΔH_{ph-ch} from a water calorimeter	No
1981-Arndt PE[27]	U. Western Australia (AU)	Naphtalene 81°C	DSC apparatus	220 (30-120°C)	DSC	Long term
1984-Kimura H[28]	Mitsubishi Eco (Japan)	CaCl$_2$.6H$_2$O with NaCl or NaF 30°C	Two tubes with water circulation	1000 (8-35°C)	Solidification temperature	No
1984-Wada T[29]	Matsushita EICo (Japan)	Na (CH$_3$COO).3H$_2$O 58°C	Thermal bath	600 (40-70°C)	Calorimetric studies	No
1986-Benson DK[30]	SERI, Colorado (USA)	PG-NPG mixture (S-S) 77°C	DSC apparatus	732 (47-97°C)	DSC	No
1987-Ting KC[31]	U. Rutgers (USA)	Na$_2$SO$_4$.nH$_2$O+additives 32°C	Durability testing chamber homemade	1000-1300 (25-35°C)	None	Yes
1988-Kimura H[32]	Mitsubishi Eco (Japan)	Mixtures of salt hydrates <25°C	Two tubes with water circulation	1000 (10-30°C)	DSC	No
1988-Porisini FC[33]	JRC-Ispra (Italy)	Hydrated Salts 15-32°C	Thermostatic chamber	up to 5650 (4-40°C)	Temperature-time curve	No
1992-Hadjieva M[34]	Bugarian AC (Bulgaria)	Paraffins 44-51°C	Thermal bath	900 (28-70°C)	DSC	No
1994-Hasan A[35]	U. Birzeit (Israel)	Fatty acids: stearic, myristic, palmitic 69°C, 58°C, 55°C	Two thermostatic baths (normal) Oven at constant temperature (severe)	450, normal (20-80°C) 21, severe (20-150°C)	DSC	No
1998-Dimaano N[36]	U. SantoTomas (Philippines)	Capric/lauric acids mixtures 13-23°C	Thermal bath	120 (10-26°C)	Temperature-time curve	No
1999-Sharma SD[37]	U. Devi Ahilya (India)	Stearic, acetamide, paraffin wax 69°C, 81°C, 54°C	Electric hot plate with T controller	300 (RT − T_{ph-ch} + 10/25°C)	DSC, weight change	Yes
2001-Sharma A[38]	U. Devi Ahilya (India)	Urea 133°C	Electric hot plate with T controller	50 (RT − 145°C)	DSC	Yes
2002-Sharma A[39]	U. Devi Ahilya (India)	Stearic, acetamide, paraffin wax 69°C, 81°C, 54°C	Electric hot plate with T controller	1500 (RT − T_{ph-ch} + 10/25°C)	DSC	Yes
2003-Nikolic R[40]	Institute Vinca (Yugoslavia)		DSC apparatus	50 (10-60°C)	DSC	No

TABLE 1 (Continued)

Year-Author Reference	Institution (Country)	PCM $T_{ph\text{-}ch}$	Thermal Cycling Characteristics			
			Experimental Set-up	No. of Cycles (T interval)	PCM Evaluation	Accelerated Test?
		Fatty acids esters eutectic mixtures and composites with gypsum 20-24°C				
2003- Sari A[41]	U. Gaziosmanpasa (Turkey)	Fatty acids 43-62°C	Thermostatic chamber	1200 (up to $T_{ph\text{-}ch}$ + 15°C)	DSC	Yes
2003-Sari A[42]	U. Gaziosmanpasa (Turkey)	Fatty acids 43-62°C	Thermostatic chamber	910 (up to 70°C)	DSC	Yes
2004-Sari A[43]	U. Gaziosmanpasa (Turkey)	Fatty acids eu-mixtures 69-42°C	Thermostatic chamber	360 (up to $T_{ph\text{-}ch}$ + 13°C)	DSC	Yes
2005-Sari A[44]	U. Gaziosmanpasa (Turkey)	Fatty acids eu-mixtures 69-42°C	Thermostatic chamber	1460 (up to $T_{ph\text{-}ch}$ + 13°C)	DSC	Yes
2006-Shilei L[45]	U. Tianjin (China)	Capric/lauric acids eu-mixtures in wallboards of gypsum 21°C	Electric hot plate with temperature controller	360 (RT − T > $T_{ph\text{-}ch}$)	DSC	Yes
2006-Özonur Y[46]	Çukurova University (Turkey)	Coco fatty acid encapsulated with gelatine-gum Arabic 30°C	Water bath	50 (22-24°C)	DSC, FTIR	No
2007-Sun JQ[47]	U. T. Guangdong (China)	AlMgZn alloy 450°C	Thermostatic chamber	1000 (442-455°C)	DSC	No
2008-Karaipekli A[48]	U. Gaziosmanpasa (Turkey)	Capric/myristic/perlite 21°C	Thermal Cycler BIOER with two water baths	5000 (not said)	DSC, FTIR	Yes
2008-Shukla A[49]	U. Devi Ahilya (India)	Organic and inorganic PCMs 58-118°C	Oven at constant temperature	600-1500 (RT − $T_{ph\text{-}ch}$ + 10°C)	DSC	No
2009-ElSebaii AA[50]	U. King Abdul Aziz (Saudi Arabia)	MgCl$_2$.6H$_2$O and acetanilide 111°C, 113°C	Oven with cooling fan for solidification and controlled temperature and heating rate	500 (40-150°C)	DSC	Yes
2009-Sari A[51]	U. Gaziosmanpasa (Turkey)	Palmitic acid/EG 61°C	Thermal Cycler BIOER with two water baths	3000 (not said)	DSC, FTIR	No
2010-Wu S[52]	South China University (China)	Paraffin/Cu-nano particles 58-60°C	Two thermostatic water baths	100 (30-70°C)	DSC	No

(Continues)

TABLE 1 (Continued)

Year-Author Reference	Institution (Country)	PCM T_{ph-ch}	Thermal Cycling Characteristics			Accelerated Test?
			Experimental Set-up	No. of Cycles (T interval)	PCM Evaluation	
2011-ElSebaii AA[53]	U. King Abdul Aziz (Saudi Arabia)	$MgCl_2 \cdot 6H_2O$ 111°C	Oven with cooling fan for solidification and controlled temperature and heating rate	1000 (40-150°C)	DSC	Yes
2011-Zuo J[54]	U. T. Dalian (China)	Caprylic acid/dodecanol 18-25°C	Thermostatic chamber	120 (Above/below T_{ph-ch})	DSC	Yes
2013-Gao E[55]	US Army (ERDC-CERL) (US)	Different commercial PCMs for building insulation 14-22°C	Weathering chamber	5400 (−10-60°C)	DSC	Yes
2013-Huang J[56]	U. Tianjin (China)	Fatty acids eu-mixtures composites 18-34°C	Two thermostatic water baths	1000 (10-45°C)	DSC	Yes
2013-Silakhori M[57]	U. Malaya (Malaysia)	Microencapsulated paraffin wax with polyaniline 53°C	Small container with heater and cooler	1000 (30-80°C)	DSC, FTIR, SEM	Yes
2014-Konuklu Y[58]	Nigde University (Turkey)	Microencapsulated caprylic acid with polyethylacrylate 13.3°C	Thermal Cycler BIOER TC-25/H	400 (not said)	DSC	No
2014-Solé A[59]	U. Lleida (Spain)	D-mannitol, myo-inositol, galactitol 165°C, 224°C, 188°C	DSC apparatus	50 (50-220°C, 260°C)	DSC, FTIR	No
2014-Zhong L[60]	U. D. T. Beijing (China)	$LiNO_3$/KCl-EG, $LiNO_3$/ $NaNO_3$-EG $LiNO_3$/NaCl-EG composites 166°C, 194°C, 208°C	DSC apparatus	100 ($T_{ph-ch} \pm 50$°C)	DSC, XRD, SEM	No
2015-Bayón R[61]	CIEMAT (Spain)	Organic PCMs 159-172°C	Oven with controlled temperature and natural cooling	up to 50 (100-185°C)	DSC, HPLC, FTIR	No
2015-RaamDheep G[62]	U. Pondicherry (India)	Benzamide, sebacic acid 123°C, 134°C	Electric hot plate with temperature controller	1000 (RT − 150°C, 160°C)	DSC	Yes
2016-Liu Z[63]	U. Sichuan (China)	Polyurethane polymers (PEG-CO) (S-S) 40-50°C	High-low temperature chamber	100 (20-90°C)	DSC, FTIR	Yes
2016-Rodriguez MM[64]	CIEMAT (Spain)	D-mannitol 165°C	Oven under inert atmosphere with	50 (100-190°C)	Sample colour, VisUV	No

TABLE 1 (Continued)

Year-Author Reference	Institution (Country)	PCM T_{ph-ch}	Thermal Cycling Characteristics		PCM Evaluation	Accelerated Test?
			Experimental Set-up	No. of Cycles (T interval)		
			controlled temperature and natural cooling			
2016-Sharma RK[65]	U. Malaya (Malaysia)	PEG 6000 56°C	Small container with heater and cooler	1500 (40-90°C)	DSC, FTIR	Yes
2016-Bayón R[66]	CIEMAT (Spain)	Liquid crystal (L-L) 250°C	DSC apparatus	11 (23-270°C)	DSC	No
2016-Diarce G[67]	U. País Vasco (Spain)	NaNO$_3$/urea eutectic 85°C	DSC apparatus	210 (10°C–95°C)	DSC	Yes
2016-Geng L[68]	South China U. Technol. (China)	n-dodecanol SiO$_2$ encapsulated 21°C	DSC apparatus	100 (−15-55°C)	DSC	No
2017-Han L[69]	Chinese Ac.Sci.(China)	lauric acid/hexanediol 33°C	Thermal bath heated and refrigerated	1000 (not said)	DSC, FTIR	Yes
2017-Huang Z[70]	U. T. South China (China)	LiNO$_3$/KCl-EG composites 165°C	Thermostatic air chamber	500 (150-180°C)	DSC	Long-term
2017-Jiang Y[71]	CSIRO (Australia)	Na$_2$CO$_3$-Li$_2$CO$_3$ 498°C	Oven	500 (400-600°C)	DSC	Long-term
2017-Liu M[72]	U. South Australia (AU)	eu-NaCl/NaCO$_3$ 635°C	Oven	1000 (600-650°C)	DSC	No
2017-Rodriguez MM[73]	CIEMAT (Spain)	Hitec (NaNO$_3$–KNO$_3$–NaNO$_2$; 7/53/40 w%) 142°C	Oven under inert atmosphere with controlled temperature and natural cooling & oven with controlled heating and cooling	up to 60 (40-170°C)	DSC, ionic chromatography	No
2017-Lao X[74]	Ceram. Inst. Jingdezhen (China)	Al/Si + SiCw/Al$_2$O$_3$ 575°C	Oven	100 (400-900°C)	SEM, EDS, TGA/DSC, XRD	No
2017-Patel J[75]	US Army (ERDC-CERL) (US)	POSO-bio-based-PCM in cubic poaches of a blanket (palm oil + soy oil) 26°C	Weathering chamber	5400 (−10-60°C)	DSC, TGA, SEM, FTIR	Yes
2017-Ramakrishnan S[76]	U. T. Swinburne (AU)	Paraffin/EPO composite 25°C	Homemade test device inside a weathering chamber	1000 (0-40°C)	DSC and mechanical strength	Yes
2017-Sami S[77]	Isfahan TU (Iran)	Paraffin/TiO$_2$ composites 60°C	DSC apparatus	80 (30-90°C)	DSC-FE-SEM, k	No
2017-Sari A[78]	T. U. Karadeniz (Turkey)			5000 (not said)	DSC, FTIR	Yes

(Continues)

TABLE 1 (Continued)

Year-Author Reference	Institution (Country)	PCM T_{ph-ch}	Thermal Cycling Characteristics		PCM Evaluation	Accelerated Test?
			Experimental Set-up	No. of Cycles (T interval)		
		SMA-graft-PEG copolymers (S-S) 40-45°C	Thermal Cycler BIOER with two water baths			
2017-Wei H[79]	U. Fuzhou (China)	Fatty acids eu-mixture with Al$_2$O$_3$-vermiculite 28°C	Thermostatic chamber	200 (RT – 70°C)	DSC	No
2017-Sun N[80]	School of Chemical Engineering of Nanjing (China)	Paraffin-PMMA/BN/TiO$_2$ 53-54°C	Oven	100 (20-80°C)	DSC, SEM	No
2017-Beyhan B[81]	Çukurova University (Turkey)	Microcapsules of capric-myristic acid with methylacrylate co-polymers 92-97°C	Not said	1000 (not said)	DSC, FTIR	No
2017-Wang[82]	Chinese Academy of Sciences (China)	Composites of caprylic-nanoic acid/EG 8°C	DSC apparatus	100 (−25-35°C)	DSC	Yes
2017-Kong W[83]	U. Sichuan (China)	PEG-PAPI mixtures (S-S) 40-50°C	High- to low-temperature chamber	100 (20-90°C)	DSC, FTIR	Yes
2017-Du X[84]	U. Sichuan (China)	HBP-PEG copolymer (S-S) 50-60°C	High- to low-temperature chamber	100 (20-90°C)	DSC	Yes
2018-Zhang X[85]	Chinese Academy of Sciences (China)	CaCl$_2$.6H$_2$O/diatomite/paraffin 28°C	DSC apparatus	100 (not said)	DSC	No
2018-Ma L[86]	South China University (China)	eu-lauric-myristic/WF 34°C	Heating chamber and refrigerator	500 (−10-60 °C)	DSC	No
2018-Gao X[87]	China Academy of Engineering Physics (China)	Nano-SiO$_2$/PW/EG 51.6°C Nano-SiO$_2$/PW/EG/HTPB 43-47°C	High- to low-temperature test chamber	500 (25-75°C)	DSC	Yes
2018-Yang Y[88]	U. Sichuan (China)	PEG-MDI-xylitol (S-S) 20-45°C	High- to low-temperature chamber	100 (20-90°C)	DSC, FTIR	Yes
2018-Zhang N[89]	China Aerodynamics R&D Center (China)	Pentaglycerine/EG (S-S) 82°C	DSC apparatus	100 (not said)	DSC	Yes

Abbreviations: BN, boron nitride; CO, castor oil; DSC, differential scanning calorimetry; EDS, energy dispersive scanning; EG, expanded graphite; EPO, expanded perlite; FE-SEM, field emission scanning electron microscopy; FTIR, Furrier transform infrared spectroscopy; HBP, hyperbranched polyol; k, thermal conductivity; HPLC, high performance liquid chromatography; HTPB, hydroxyl terminated polybutadiene; L-L, liquid-liquid transition; MDI, diphenyl-methane diisocyanate; NPG, neopentyl glycol; PAPI, polyaryl polymethylene isocyanate; PEG, polyethylenglycol; PG, pentaglycerine; PMMA, poly(methyl methacrylate); POSO, palm oil + soya oil; PW, paraffin wax; SEM, scanning electron microscopy; RT, room temperature; S-S, solid-solid transition; TGA, thermogravimetric analysis; VisUV, visible and ultraviolet spectroscopy; XRD, X-ray diffraction; WF, wood flour.

Almost all references shown in Table 1 report on tests based on consecutive heating/cooling cycles. Only in a few cases,[28,29,32,36,55,72-74] a stand-by time at constant temperature between the ramps was introduced. The usual temperature interval for the cycles was 10°C to 30°C above/below T_{ph-ch}, and only a handful of researchers carried out tests with larger temperature intervals.[27,35,50,53,71,74] The number of cycles ranged from 11 to 5650, although most authors performed up to 1500 cycles and only a few of them attained 3000 or 5000 cycles. For those materials that degraded upon thermal cycling, a decrease in ΔH_{ph-ch} was normally observed. In this sense, organic PCMs with T_{ph-ch} values below 100°C, such as paraffins or fatty acids, showed a decrease in ΔH_{ph-ch} not higher than 10% after 450 to 1200 cycles.[34,35,42,56] This decrease in ΔH_{ph-ch} was lower or even disappeared when the same PCMs formed composites with inert materials.[45,48,51,76,77] In contrast, other organic PCMs with T_{ph-ch} above 100°C such as sugar alcohols,[61,64] hydroquinone,[61] salicylic acid,[61] benzamide,[62] or liquid crystals[66] showed strong degradation after only a few melting/freezing cycles. For the case of solid-solid PCMs, only a slight decrease (less than 4%) in ΔH_{ph-ch} was observed after the cycles.[30,63,78,83,84,88] Hydrated salts, such as $CaCl_2.6H_2O$,[50] $Na_2SO_4.10H_2O$,[26] or $NaCH_3COO.4H_2O$,[29] showed a strong decrease (up to 70%) in ΔH_{ph-ch}, in addition to the occurrence of incongruent melting/freezing phenomena. Sometimes, the use of additives[26] or the so-called water principle[53] reduced that ΔH_{ph-ch} decrease. PCMs for high temperature applications (greater than 300°C) showed no degradation upon cycling (inorganic salts[60,70-73]) or a slight decrease in ΔH_{ph-ch} (metallic alloys[47,74]).

The large scattering in the test conditions chosen by the different authors is evident from this literature review, especially in relation to the temperature interval and the number of cycles performed. In many of the references gathered in Table 1, the thermal cycles were considered accelerated tests without any previous justification (see the right-hand column of the table). Under this assumption, some authors established correlations between the number of thermal cycles and the period of real operation. Since reasons were never given for such extrapolations, the variety of correlations is wide: Raam Dheep et al[62] stated that 1000 cycles were equivalent to 4 years of real operation; for Sharma et al,[65] 1500 cycles were equivalent to 5 years of operation, whereas Gao et al[55] and Patel et al[75] claimed that the stability of the PCMs tested could be ensured for 20 years after enduring 5400 cycles in a weathering chamber.

According to the methodology followed in other branches of science,[90-97] accelerated tests require previous material lifetime relationship models and a comparison with the results obtained under service conditions, which is not the case of the tests shown in Table 1 and proclaimed as accelerated. These tests were performed in a relatively short time, but this does not mean that they accelerated the degradation process of the material. Cycling tests are certainly useful because they give an idea of the short-term stability of PCMs, but extrapolating their results to long-term operation under real working conditions without any further justification seems rather inaccurate. In authors' opinion, this misunderstanding is mainly due to fact that no testing protocols exist for validating storage materials; for which reason, authors have applied their own criteria not only for the testing procedures but also for predicting the material behaviour under long-term operation.

The objective of this paper is, therefore, to present a full methodology for validating storage media, focusing the attention on PCMs. This methodology consists of a set of stages that should lead to the assessment of a certain PCM for a specific application. The successive steps to be followed and the kind of tests that could be performed will be discussed along the paper. Key concepts of the methodology such as control properties, service conditions, degradation factors, preliminary assessment tests, and accelerated life testing will be described as well. It is important to remark that the methodology proposed in this paper is intended as an initial guideline that could be used not only for validating PCMs but also for other kinds of thermal energy storage media.

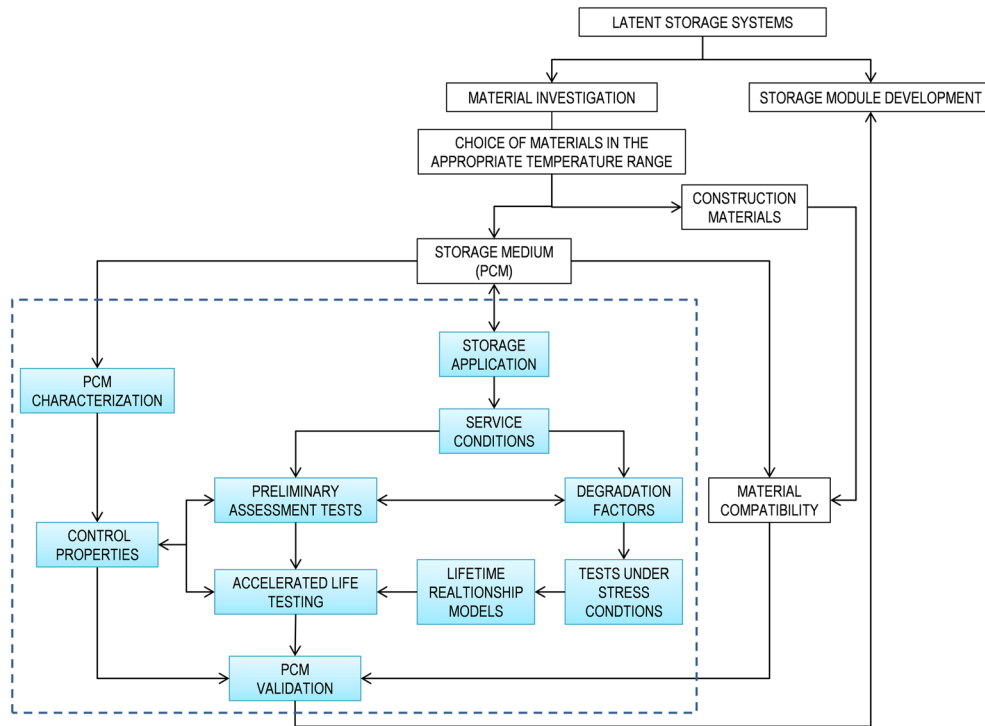## 2 | PROPOSED METHODOLOGY FOR PCM VALIDATION

The methodology for PCM validation proposed in this paper starts off the scheme presented by Abhat[98] in 1983. This scheme (Figure 2) comprised the different stages that may be involved in the design of a storage system, in that case, a latent storage system for solar thermal applications. According to it, the material investigation side included the selection of the storage material (PCM in this case) based not only on its thermophysical properties and melting/freezing characteristics but also on its compatibility with the construction materials. The study of the PCM short-term, long-term, and thermal cycling behaviour is proposed to achieve the, so-called, long life consideration.

Using the flowchart of Abhat[98] under the material investigation side as point of departure, the new methodology displayed inside the dashed line of the scheme of Figure 3 is proposed. This new methodology joins thermophysical properties and melting/freezing characteristics in a single step called PCM characterization. The short-term behaviour, long-term behaviour, and thermal cycling tests are merged into a preliminary
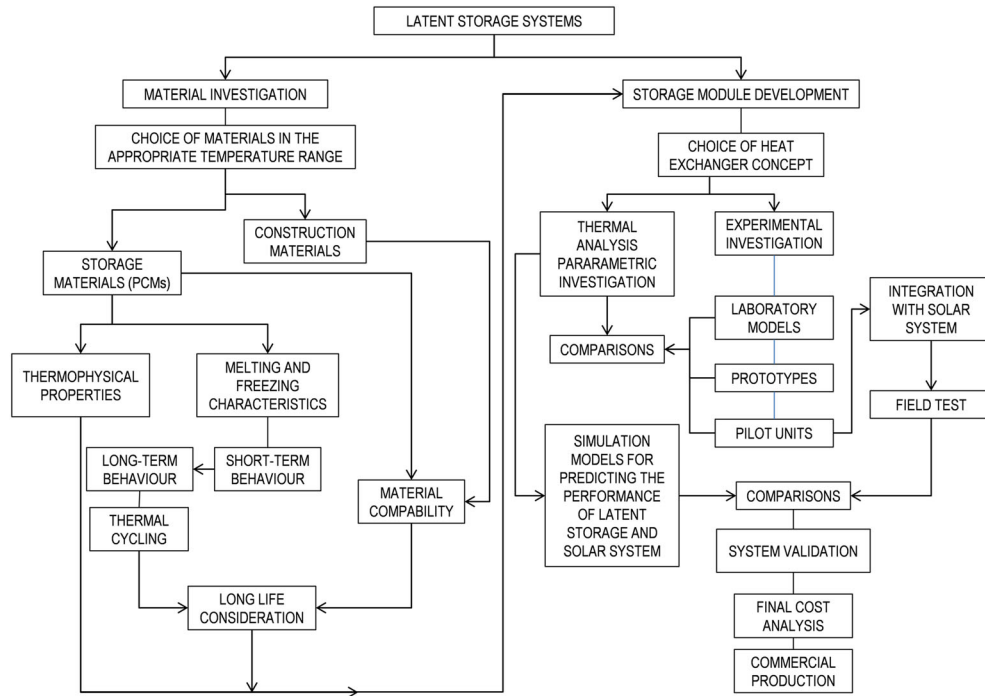
FIGURE 2 Flowchart providing an overview of the different steps involved in the development of a latent storage system[96] [Colour figure can be viewed at wileyonlinelibrary.com]

FIGURE 3 Scheme of the proposed methodology for validating PCMs as latent storage media [Colour figure can be viewed at wileyonlinelibrary.com]

assessment tests stage to be performed prior to the accelerated life testing stage, which finally leads to the PCM validation. It is important to mention that PCM validation also requires compatibility studies with the materials in contact, which are the construction materials of the storage module or other structures such as fins,

extended surfaces, and shells. However, this paper will only focus on the validation of PCMs as storage media, and hence, material compatibility tests will not be here considered.

In the next sections, the different steps of the proposed methodology for PCM validation will be described and discussed in more detail. We would like to highlight that the approach followed in this methodology would be equally valid for materials to be used as sensible or thermochemical storage media.

3 | PCM CHARACTERIZATION AND CONTROL PROPERTIES

The main thermophysical properties that make a material a potential latent storage medium (PCM) are its phase-change[18] temperature ($T_{\text{ph-ch}}$) and enthalpy ($\Delta H_{\text{ph-ch}}$). The analytical methods most commonly used for obtaining those properties are DSC and what is known as the T history method. The first method is commercially available in two types of equipment: differential scanning calorimeters and thermobalances, which can perform simultaneously both TGA and DSC. As for the T-history method, it is always carried out in set-ups specifically designed for such a purpose. Although there are other thermophysical properties that could be used for PCM characterization (density, heat capacity, thermal conductivity of the different phases, viscosity of the liquid phase, etc), it was discussed in Section 1 that almost all authors measure $T_{\text{ph-ch}}$ and $\Delta H_{\text{ph-ch}}$ for detecting any changes in the PCM performance. Therefore, these two thermophysical properties can be established as control properties, and hence, they should be measured before and after each set of tests.

In the following subsections both types of thermal analysis methods (DSC and T history) will be shortly described and their advantages and disadvantages in terms of PCM characterization highlighted.

3.1 | Differential scanning calorimetry

DSC is a standard method for thermal analysis in which the heat flow between a sample and the environment is calculated and recorded as temperature increases or decreases at constant rate. Heating/cooling velocity is usually in the range of 0.5°C/min to 10°C/min, the amount of mass analysed is about 5 to 20 mg, and the measurements are performed under inert atmosphere (usually N_2 or Ar). The resulting data are curves representing either specific heat flow (W/g) or enthalpy (J/g) vs temperature. From any of these curves, phase change temperatures and enthalpies can be obtained for the different phase transitions undergone by the material

under study. Some DSC devices also allow measuring heat capacity, C_p, in solid and liquid states.

Although the DSC technique is quite accurate and provides quick and reliable results, it presents some issues associated to sample size and heating/cooling rates. On the one hand, because of the small sample size, the supercooling phenomenon is promoted,[99] while the degree of phase segregation (ie, incongruent melting/freezing) is diminished.[98] On the other hand, if heating rate is very high, heat flux may not be observed at the correct temperature because of a temperature gradient inside the sample. This is especially important in materials with poor thermal conductivity and large phase-change enthalpy. Observed supercooling and phase segregation phenomena are closer to the real ones if the sample amount is larger, but in that case, temperature gradients inside the sample may be of importance. Decreasing the heating rate reduces those gradients, but it also reduces the signal/noise ratio and hence the measurement precision.[100] In short, DSC measurements are strongly affected by the experimental conditions, and therefore, they may not be representative enough of the bulk PCM behaviour. This is also the reason why it is difficult to compare the results obtained by different authors that use different DSC or TGA/DSC equipment and procedures. In this sense, it is worth mentioning the task 42/29 of the IEA SHC/ECES TCPs, where a standard procedure for PCM characterization using DSC has been proposed.[101] This public document is based on the standard[102] RAL-GZ 896 and not only defines how DSC apparatus should be calibrated and how samples should be prepared but also contains a detailed description of the methodology and several suggestions for improving the accuracy of results. Other attempts to establish some common guidelines for measuring thermophysical properties of storage media by using DSC have been carried out by the Thermal Energy Storage working group of the IEA SolarPACES-Task III TCP, in particular for determining the heat capacity of solar salt with nanoparticles.[103]

3.2 | T-history method

In the so-called T-history method, the temperature evolution with time is recorded against ambient temperature for both the PCM sample and a reference material during a cooling process. The reference material must be a substance with well-known thermophysical properties that remains in the same state (usually liquid) in the whole temperature interval of the experiment. Both sample and reference are assumed to exchange thermal energy with the environment in a similar way.

This method was proposed in 1999 by Zhang et al[104] from Tsinghua University, with the aim of obtaining

properties such as melting point, enthalpy of fusion, heat capacity, degree of supercooling, and even thermal conductivity for various PCM samples at the same time. Afterwards, both the design of the original set-up and the mathematical models applied for calculating the thermophysical properties from the experimental data have been improved by researchers of different institutions over the world.[105-115] Since the reference material most commonly used is water, T-history method has been mainly used for characterizing PCMs for latent storage applications below 100°C. In recent years, there have been some attempts to use this methodology also for PCMs working at higher temperatures, so that solid copper has been proposed as reference material.[116]

Compared with the analytical techniques for thermal analysis commercially available (DSC and TGA/DSC), T-history method presents several advantages. It allows using larger samples (approximately 10-100 g), so that the drawbacks associated to small sample size mentioned in Section 3.1 are avoided. Moreover, the experimental set-ups are simpler and do not require costly equipment such as DSC and TGA/DSC devices. According to Lázaro et al,[108] the accuracy of the thermophysical properties obtained with T-history methods is quite good because uncertainty values in the calculated enthalpy are about 10%. However, since each experimental set-up is unique, common standard methodologies for performing the experiments and for the mathematical procedure used for data analysis have not yet been defined.[117]

# 4 | SERVICE CONDITIONS AND DEGRADATION FACTORS

The specific service conditions of a storage medium are those under which the storage system is expected to work during its lifetime. For the case of a PCM, these conditions are those dealing with charge/discharge cycles (time frequency, stand-by periods, etc), temperature (upper and lower limits), atmosphere (gases in contact with the PCM), pressure (of the gases), etc. In Figure 4, the service conditions of a storage system are displayed together with the type of changes, either chemical or physical, they may produce on the medium (in this case a PCM). In most cases, these changes decrease the capability of the material to store energy so that it is said that the material is degraded and hence not stable under certain service conditions. Degradation factors affecting the storage medium are among the service conditions. Performing studies on PCM degradation is crucial since they allow obtaining the degradation kinetics, which are necessary for the design of accelerated life test.

4.1 | Chemical degradation

Chemical degradation implies that the storage medium undergoes changes in its chemical composition so that new compounds are formed through the occurrence of chemical reactions. In the working temperature range of the storage system, chemical reactions may take place because the material is unstable and dissociates into other compounds or/and it reacts with the surrounding atmosphere.

Chemical degradation of PCMs is reported in several papers under the name of thermal stability studies.[58,68-71,76-82,85-87,118-120] In all of them, TGAs are performed under inert atmosphere (N_2 or Ar) at a single heating rate (normally 10°C/min) in order to obtain the temperature limit for the beginning of PCM degradation. However, the temperature at which degradation is observed in a TGA experiment depends on the heating rate used
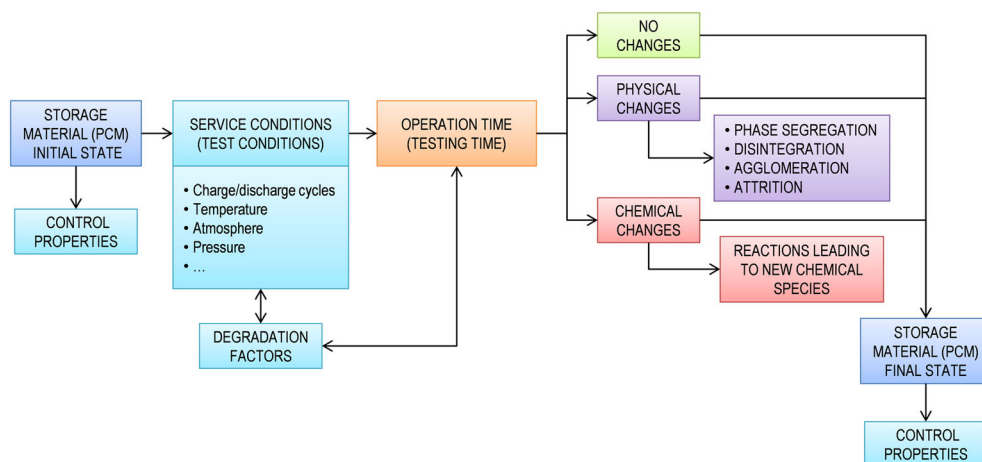
FIGURE 4 Scheme showing the service conditions of a storage system and the changes they may produce in the storage material, in this case a PCM [Colour figure can be viewed at wileyonlinelibrary.com]

because reaction kinetics are temperature dependent. Hence, if PCM stability wants to be predicted, the kinetics of its degradation processes must be studied. Moreover, as will be discussed in Section 6, degradation kinetics are required for obtaining the lifetime relationship models required for designing accelerated life tests. For that purpose, TGA apparatus is a very powerful tool since it allows performing kinetic analysis of thermal measurements in a very accurate way. An example of this kind of analysis can be found in the paper of Tong et al,[121] which reports on D-mannitol decomposition studied under nonisothermal conditions by performing TGA at different heating rates.

4.2 | Physical degradation

A storage medium undergoes physical degradation if it maintains the chemical composition but presents changes that have a negative effect on its performance. Signs of physical degradation can be phase segregation, disintegration, agglomeration, attrition, etc. This kind of degradation is most commonly found in solid materials used in sensible storage or in thermochemical storage, but it can also happen to PCMs. Hydrated salts used as PCMs may undergo phase segregation, because the water released during melting cannot dissolve all the salt, so there is some remaining solid that separates and settles at the bottom of the container because of its higher density. During the reverse process, both water and settled salt are unable to crystallize together again. This phenomenon is known as "incongruent melting/freezing" and implies a decrease in the stored energy density after several charge/discharge cycles.[122]

Another example of phase segregation in latent storage materials occurs when they are combined with other materials forming composites or are embedded in porous structures.[118] The aim of combining PCMs with other materials (normally solids with a higher thermal conductivity than the PCM) is enhancing heat transfer by increasing the effective thermal conductivity. However, if PCM segregation occurs upon thermal cycling (mainly while PCM is melted), the desired improvement in thermal conductivity is lost.

5 | PRELIMINARY ASSESSMENT TESTS

Once a material has been chosen for a storage application on the basis of its main thermophysical properties, some preliminary assessment tests are required (see Figure 3). The aim of these tests is, on the one hand, to determine which service conditions are degradation factors and, on the other hand, to evaluate the short-term behaviour of the PCM for deciding whether it can be considered or not as potential storage medium for a certain application.

Preliminary assessment tests include tests under conditions as close as possible to the real working ones in terms of temperature range, heating/cooling rates, atmosphere in contact with the PCM, number of cycles, stand-by times, etc (see Figure 4). Moreover, samples in the order of grams or even kilograms are desirable so the results are representative enough. For evaluating the PCM state, control properties (T_{ph-ch} and ΔH_{ph-ch}) are measured, at least, at the end of the tests in order to check whether their value has changed and, if so, to which extent.

Examples of preliminary assessment tests could be the consecutive thermal cycles carried out in the majority of references in Table 1. As discussed in Section 1, although there is a common trend to rely on thermal cycling for evaluating the behaviour of PCMs, the authors have never argued the criteria for choosing the experimental conditions of the tests. In Table 1, the PCMs were monitored by measuring the evolution of the control properties after a certain number of cycles or at the end of the cycling tests. In general, those materials degrading upon thermal cycling showed a decrease in ΔH_{ph-ch}, the extent of which strongly depended on the kind of PCM studied. Despite the large amount of papers dealing with this subject, no criterion has ever been stablished in terms of what ΔH_{ph-ch} decrease defines the thermal stability of a PCM.

Sometimes, a PCM is able to stand a certain number of consecutive cycles with almost no changes in the control properties,[59] but it degrades when it is kept melted for a while.[123] This is because, in the case of PCMs, temperature is usually the main degradation factor leading to chemical changes. In contrast, melting/freezing processes themselves are more likely to produce phase segregation or incongruent melting/freezing, which implies physical degradation. This proves that consecutive thermal cycling tests are not enough for taking a first decision about the feasibility of a PCM, since they underestimate the effect of temperature when the material is melted.

In authors' opinion, common criteria for designing preliminary assessment tests for PCMs need to be adopted. These criteria should include guidelines for defining the experimental conditions of the tests in relation to the specific service conditions of the storage system. In this respect, the question remains open to the R&D community, and it would be desirable to achieve some degree of consensus. Additionally, it might be worth stablishing the limits to the variation of the control properties after the tests to decide whether a certain PCM is assumed to pass or not these preliminary assessment

tests. This would imply analysing to which extent the variation of the control properties is relevant to the performance of the whole storage system.

6 | ACCELERATED LIFE TESTING

By definition, accelerated life testing consists of a set of methods intended to ensure product reliability during design and manufacturing and after product fielding. In all accelerated testing procedures, stress is applied to promote failure[90] so that, by the term accelerated, a shortened time to failure is implied. If the objective is to use accelerated testing to predict product lifetime, the stress must produce the same degradation and failure types that would be encountered during the intended use of the product. Therefore, accelerated life tests are usually applied to products, systems, or components prior to their commercial implementation. The general methodology for accelerated life testing was described in the literature already[91] in the 70s. This methodology has been improved over the years and adapted to different products used in specific applications (materials, components, systems, etc).[92-97]

Taking into account the methodologies already developed for accelerated life testing, a detailed scheme has been elaborated with the different stages to be followed (see Figure 5). The first stage is the identification of the degradation factors or stress variables that are associated

to certain service conditions. As previously mentioned, degradation factors have been already determined by preliminary assessment tests. The next stage involves tests under increasing stress levels of those degradation factors so that analytical models for lifetime relationships can be obtained from experimental data. These models stablish the degradation rate of the material for each degradation factor and each stress level. In order to find out appropriate correlations between accelerated testing results and real lifetime behaviour, tests under real working conditions are required. The degradation state of the PCM after each set of tests has to be monitored by measuring the appropriate control properties.

The kind of lifetime relationship model used for fitting the experimental data obtained under stress conditions depends on the degradation factor that is considered.[124] The Arrhenius model is the most commonly used when temperature is the degradation factor and a chemical reaction occurs. This is because Arrhenius equation gives the dependence of the kinetic rate constant of a chemical reaction, k, on the absolute temperature, T, a preexponential factor, A_0, the activation energy for the reaction, E_a, and the universal gas constant, R.

$$k(T) = A_0 e^{-\frac{E_a}{RT}}. \tag{1}$$

The so-called Eyring models are very appropriate when temperature combines with other degradation factors, such as mechanical stress (Weertmann model),
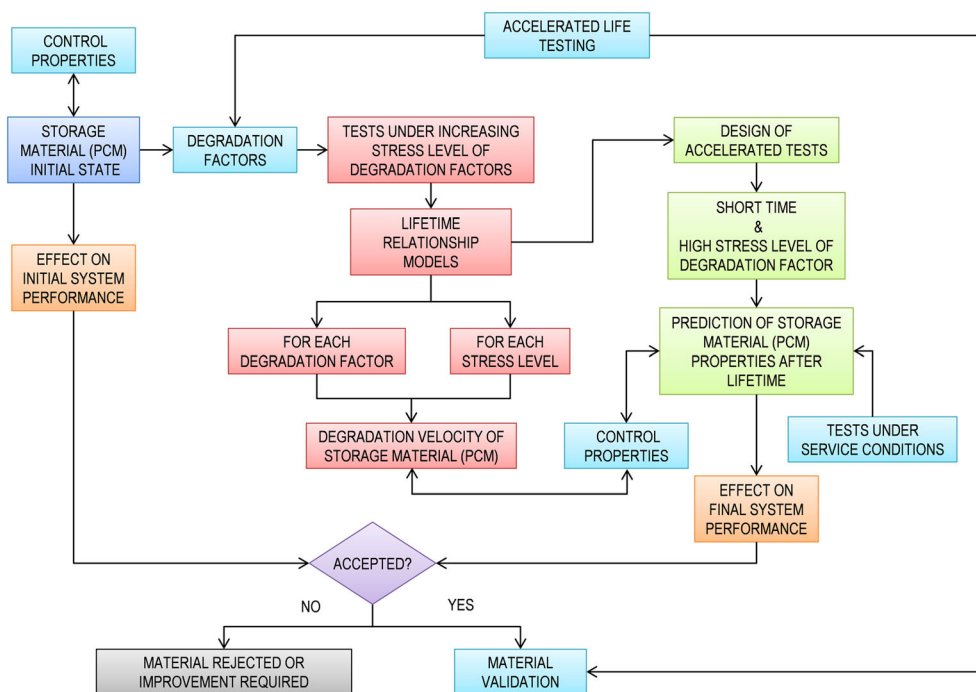
FIGURE 5 Scheme showing the accelerated life testing methodology applied to storage materials, in this case to PCMs [Colour figure can be viewed at wileyonlinelibrary.com]

moisture (Pecks model), or electrical current density (Blacks model).[124] If temperature combines with voltage, the Kemeny model is usually adopted. For other degradation factors associated to mechanical fatigue damage, analytical models such as Miner Rule or Coffin-Manson inverse power law have been proposed.[124] Miner's hypothesis does not describe any physical or chemical change mechanism and only attempts to describe how damage accumulates. It also assumes that all damage increments add up independently, so that no synergistic mechanisms are considered. Depending on the kind of material or product requirements, lifetime relationship models can be formulated in different ways. They may be expressed as control property variation over time for different stress levels, failure time as a function of stress level, etc.[90,124]

As said above, the lifetime relationship models applied when temperature is the degradation factor are based on Arrhenius equation. This is because in such case, a chemical reaction takes place, and hence degradation is governed by the reaction kinetics. Unfortunately, literature hardly includes papers reporting on degradation kinetics of storage media. In relation to PCMs, only a few kinetic studies have been published and all of them dealing with D-mannitol degradation. One is the study published by Tong et al,[121] already mentioned in Section 4.1, in which the kinetics of D-mannitol decomposition was studied by TGA. Another one is the work reported by Sagara et al,[125] in which D-mannitol was tested in a DSC apparatus at constant temperature above melting point and the variation of latent heat over time was used for obtaining the degradation kinetics. Bayón et al studied D-mannitol degradation also at constant temperature (T_{ph-ch} + 15°C), but in their case, ovens under either air[123] or inert gas (N$_2$ or Ar) atmosphere were used.[62] For monitoring degradation, they measured sample mass loss and analysed the remaining amount of D-mannitol by HPLC, observing that this PCM degraded very quickly even under inert atmosphere.

These papers aimed to obtain the degradation kinetics of D-mannitol and not lifetime relationship models; however, the results of one of them will be here used for illustrating how this kind of can be obtained using Arrhenius equation (Equation 1). In particular, we will take the results reported by Sagara et al,[125] who studied D-mannitol degradation kinetics in a DSC apparatus under isothermal conditions by monitoring the variation of latent heat (ie, phase change enthalpy). These authors defined the conversion degree, α (ie, the fraction of original material that has reacted) as a function of latent heat variation (decrease) in relation to its initial value through the expression:

$$\alpha = 1 - \frac{(\Delta H_{ph-ch})_t}{(\Delta H_{ph-ch})_0}. \tag{2}$$

Therefore, they calculated α from DSC data and found that the experimental results were better fitted assuming a first-order mechanism for D-mannitol degradation. This means that the expression for the time variation of the conversion degree, α, at a certain temperature, T, is as follows:

$$-\ln(1-\alpha) = kt. \tag{3}$$

The fitting lead to the Arrhenius parameters is E_a = 117 kJ/mol and lnA_0 = 16.4. Using these results and choosing the latent heat ratio, $(\Delta H_{ph-ch})_t/(\Delta H_{ph-ch})_0$, as control property, the lifetime relationship model for D-mannitol has been obtained. This model gives the set of curves of Figure 6A, which represent the variation of the control property with time for different stress levels of the degradation factor (ie, temperatures above melting point, 165°C).

If a certain value of the control property is established as the limit for acceptable material performance, the expected time to failure can be plotted versus degradation factor stress level, in this case, temperature. In Figure 6B, time-to-failure curves have been represented for different values of latent heat ratios (0.9-0.75) limiting the acceptable performance of D-mannitol. For example, if only 10% decrease in latent heat is allowed (ratio = 0.9), D-mannitol could be used for about 5 months provided it is kept melted at 170°C (ie, 5°C above melting temperature). However, if the temperature is 180°C (ie, 15°C above melting temperature), this period is reduced to about 2 months. It should be pointed out that, if daily charge/discharge processes are expected, D-mannitol will remain melted, and hence, at temperatures higher than 165°C, only during the sun hours at which the storage system is charged. In terms of time, this means that it could meet the acceptable performance requirement for three times the time to failure shown in Figure 6B. Therefore, in the above examples, time to failure should be 15 and 6 months instead of the stated 5 and 2 months, respectively. However, even under this assumption, it is very clear that D-mannitol degrades very quickly and cannot be used as a storage medium for any latent system that is expected to work during several years. Actually, Bayón and Rojas[123] demonstrated that D-mannitol degradation rate under conditions closer to the service ones is even higher than the rate obtained by Sagara et al.[125]

The main advantage of lifetime relationship models is that they can be applied for predicting long-term performance of a certain material. For the case of PCMs and other materials implemented in thermal storage systems that are expected to work for several years, it is quite
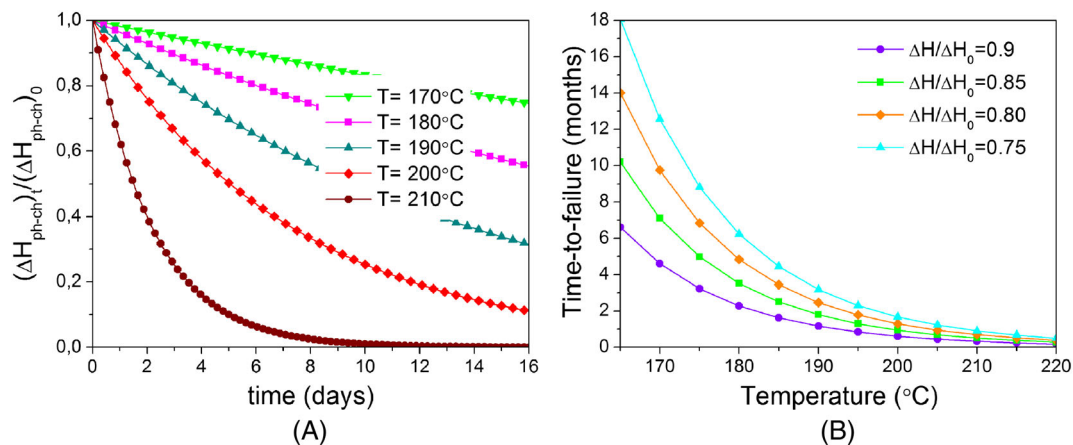
FIGURE 6 Lifetime relationship diagrams for thermal degradation of D-mannitol. Latent heat ratio vs time for different temperatures above melting point (A). Time-to-failure vs temperature for different latent heat ratios (0.9-0.75) (B) [Colour figure can be viewed at wileyonlinelibrary.com]

obvious that the time scale of the lifetime relationship diagrams must be in the order of years. In Figure 7, general lifetime diagrams similar to the ones displayed in Figure 6 have been constructed as an example by using generic stress levels and changing the Arrhenius parameters so that the time scale is increased to the range of years. It is desirable that these diagrams included as many experimental data as possible from tests under service conditions (white circles) in order to improve the estimation of the control property variation along the service lifetime (green-dashed line). In principle, the control property variation under service conditions can be estimated with the lifetime relationship equation, but it is preferable if it was validated with experimental data.

If 10% decrease of the control property ratio at the end of material service lifetime is set as an acceptable failure limit for the lifetime diagrams of Figure 7A, the time-to-failure diagram in the logarithmic scale of Figure 7B

can be constructed. Then the accelerated tests for each degradation factor are easily designed by using the corresponding time-to-failure diagram, in which stress level 0 corresponded to in-service conditions. In Figure 7B, some examples of how accelerated tests could be performed depending on the testing time available have been indicated. According to this diagram, if tests were performed under stress level 12, the material would attain the failure limit in about 3 months. However, if the tests were performed at stress level 8 (lower than stress level 12), the material would stand at least for 1 year.

There are no fixed rules for designing accelerated tests. This means that the design criteria can be chosen depending on the sort of material and its application. These criteria should establish not only the value for the accepted failure limit of the control property and hence the time-to-failure under service conditions but also the testing time and the stress level to be applied during the
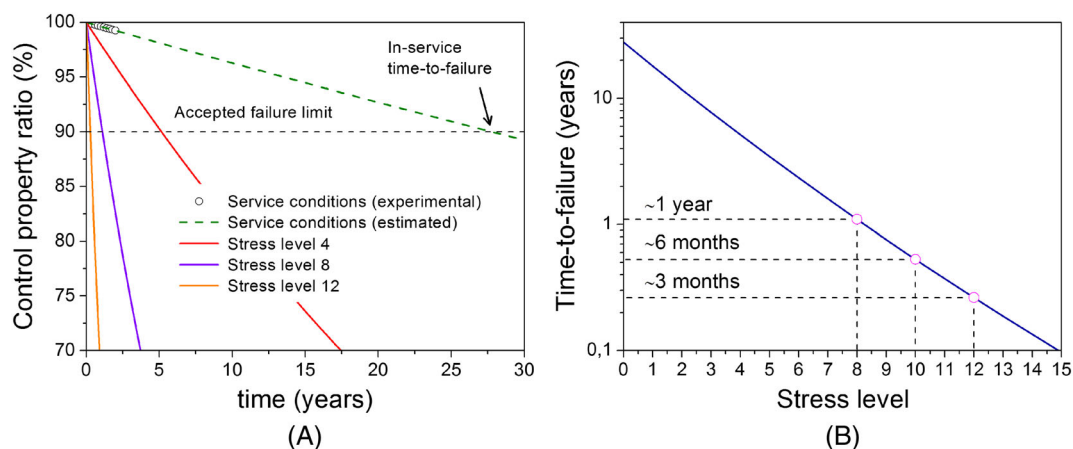
FIGURE 7 General example of a lifetime relationship model based on Arrhenius equation. Control property ratio vs time plot for different stress levels (A). Time-to-failure vs stress level plot assuming a 10% decrease of the control property as failure limit (B) [Colour figure can be viewed at wileyonlinelibrary.com]

tests. For the particular case of thermal storage materials and PCMs, the accepted failure limit for the control property (for example, $\Delta H_{\text{ph-ch}}$) has to be decided taking into account its effect on the whole system performance and how long the system is expected to be under operation. Accelerated tests may then be used not only for confirming the long-term behaviour of a storage medium but also for validating materials expected to undergo similar degradation processes.

7 | CONCLUSIONS

In this study, a full methodology for validating materials to be used as reliable latent storage media (PCMs) for a given application is proposed. This methodology considers successive stages, which include PCM characterization, the performance of preliminary assessment tests, and the design of accelerated life tests. Preliminary assessment tests are performed under conditions as close as possible to the real working ones. The design of the accelerated life tests needs lifetime relationship models based on degradation factors capable of predicting the long-term behaviour of the storage medium under service conditions. The methodology proposed aims to cover the lack of guidelines for validating PCMs, and it is expected to be a very useful tool for the whole research community in the field of latent storage materials and systems. The authors hope that this community will contribute to the further development of this methodology here proposed. It is very important to highlight that the scope of this methodology goes beyond the limited domain of latent storage media (PCMs) since a similar approach could be applied for validating materials to be used in sensible or thermochemical storage systems.

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