

ENERSTOCK 2021

15TH INTERNATIONAL VIRTUAL CONFERENCE ON ENERGY STORAGE

June 9 – 11, 2021, Ljubljana, Slovenia



**BOOK OF
ABSTRACTS**



Editors

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TABLE OF CONTENTS

Welcome Addresses	iii
Committees	iv
Scientific Programme	vii
Abstracts	1
Author Index	285



WELCOME ADDRESS

Dear participants of the Enerstock2021 conference

The 15th International Conference on Energy Storage ENERSTOCK2021 is held in Ljubljana, Slovenia from 9 to 11 June 2021 and is hosted by the University of Ljubljana - Faculty of Mechanical Engineering and the National Institute of Chemistry Slovenia.

At the conference, an impressive number of distinguished experts present the latest scientific and technological achievements as well as future trends and prospects related to materials, applications and systems for thermal and electrical energy storage, power-to-gas or heat applications, climate change and other related disciplines. In addition to two plenary and five keynote lectures, participants have the opportunity to present their work in oral presentations and short oral poster presentations.

The contributions show that the development of materials for thermal energy storage remains an important and urgent research area for the advancement of TES technologies. One third of all contributions is dedicated to new and improved TES materials, presented in 10 sessions. The same percentage is dedicated to TES applications, while Systems account for 20% of all contributions.

On behalf of International Energy Agency Technology Collaboration Programme Energy Storage, the University of Ljubljana - Faculty of Mechanical Engineering and the National Institute of Chemistry Slovenia we would like to thank you for your contributions leading to this successful conference.

Yours faithfully,



Alenka Ristić

Uroš Stritih

Alenka Ristić and Uroš Stritih

Conference organizers



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Andreas Hauer



Henrik Lund



Keynote Speakers

Luisa F. Cabeza



Claudio Gerbaldi



Wim van Helden



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PROGRAMME



WEDNESDAY, 9 JUNE 2021

9:00 – 9:50	Opening
9:00 - 9:05	Alenka Ristić and Uroš Stritih, Organizers
9:05 - 9:10	Mitjan Kalin, dean, Faculty for Mechanical Engineering, UL, Slovenia
9:10 - 9:15	Gregor Anderluh, director, National Institute of Chemistry, Slovenia
9:15 - 9:20	Hinko Šolinc, general director, Directorate of Energy <i>Ministry of Infrastructure, Slovenia</i>
9:20 - 9:35	Teun Bokhoven, Chairman Energy Storage TCP
9:35 - 9:45	Uroš Stritih, Slovenian delegate at TCP ES
9:50 – 10:40	Plenary session P1 Chairperson: Alenka Ristić
9:50 – 10:35	Plenary lecture PL 1: What is the value of energy storage? <u>Andreas Hauer</u> <i>ZAE Bayern, Germany</i>
10:35 – 10:45	Short Break
10:45 – 12:50	Morning session A1 TES applications Chairperson: Andreas Hauer
10:45 – 11:10	Keynote lecture KL1 Thermal Energy Storage: developments and results for large scale technologies and for compact technologies <u>Wim van Helden</u> <i>AEE Intec, Austria</i>
11:10 – 11:30	Development and implementation of PTES in Copenhagen <u>Christian Kok Skov</u> <i>Planenergi, Denmark</i>
11:30 – 11:50	Simulation and performance evaluation of large-scale thermal energy storage in renewables-based district heating system <u>Alice Tosatto</u> <i>University of Innsbruck, Austria</i>
11:50 – 12:10	Experimental investigation on a new highly efficient regeneration process for thermochemical energy storage <u>Henner Kerskes</u> <i>University of Stuttgart, Germany</i>



10:45 – 12:45	Morning session C1	Systems
	Chairperson: Milan Ostry	
10:45 – 11:05	Operation and characteristics of a direct contact latent thermal energy storage <u>Stefan Krimmel</u> <i>Lucerne University of Applied Sciences and Arts, Switzerland</i>	
11:05 – 11:25	Insulation with controllable heat transfer for thermal energy storages <u>Jonina Felbinger</u> <i>German Aerospace Center, Germany</i>	
11:25 – 11:45	Large heat pumps with hot water store in local heating systems - Investigation of operation strategies <u>Shengqing Xiao</u> <i>Chemnitz University of Technology, Germany</i>	
11:45 – 12:05	Vertical rock bed for high temperature energy storage: pilot plant findings <u>Kai Knobloch</u> <i>Technical University of Denmark, Denmark</i>	
12:05 – 12:25	The IEA energy storage TCP Task 36 – a working group on Carnot Batteries <u>Dan Bauer</u> <i>German Aerospace Center, Germany</i>	
12:25 – 12:45	Combined heat and power coal fired plants – the best choice of early grid-scale Carnot batteries applications <u>Vaclav Novotny</u> <i>Czech Technical University in Prague, Czech Republic</i>	
12:45 – 14:00	Sponsor chat / Break	
14:00 – 16:00	Afternoon session A2	TES applications
	Chairperson: Per Alex Sørensen	
14:00 – 14:20	Tests with PCM in grouting of UTES borehole heat exchangers <u>Burkhard Sanner</u> <i>Ubeg Dr. Mands & Sauer GbR, Germany</i>	
14:20 – 14:40	Integrated energy systems using phase change materials as storage medium – experience from Norwegian installations. <u>Kirsti Midttømme</u> <i>Norce Norwegian Research Centre, Norway</i>	



14:40 – 15:00	Long-term performance of PP-HTR liners for pit thermal energy storages <u>Gernot M. Wallner</u> <i>University of Linz, Austria</i>
15:00 – 15:20	Design and construction of an active latent thermal energy storage system <u>Alberto Egea Villareal</u> <i>Polytechnic University of Cartagena, Spain</i>
15:20 – 15:40	Design aspects for large-scale pit thermal energy storage <u>Thomas Schmidt</u> <i>Solites - Steinbeis Innovation gGmbH, Germany</i>
15:40 – 16:00	Utilisation of ice storage systems in Slovenia <u>Urška Mlakar</u> <i>University of Ljubljana, Slovenia</i>
14:00 – 16:05	Afternoon session B2 EES materials Chairperson: Robert Dominko
14:00 – 14:25	Keynote lecture KL2 An overview on hybrid polymer electrolytes for next-gen solid-state batteries operating at ambient temperature <u>Claudio Gerbaldi</u> <i>DISAT, Politecnico di Torino, Italy</i>
14:25 – 14:45	Electrochemical degradation of carbon-supported gold nanoparticles <u>Milutin Smiljanić</u> <i>National Institute of Chemistry, Slovenia</i>
14:45 – 15:05	Unique solid carbonate-based single ion conducting block copolymer for high-voltage lithium metal batteries <u>Gabriele Lingua</u> <i>DISAT, Politecnico di Torino, Italy</i>
15:05 – 15:25	Development of a PCM-composite for the thermal management of Li-ion batteries <u>Sebastian Gamisch</u> <i>Fraunhofer Institute for Solar Energy Systems ISE, Germany</i>
15:25 – 15:45	Composite polymer membranes as electrolytes for lithium-based batteries <u>Marisa Falco</u> <i>DISAT, Politecnico di Torino, Italy</i>
15:45 – 16:05	Effective radial thermal conductivity measurements of cylindrical battery cells based on the heat flow meter method – a method validation approach <u>Daniel Lager</u> <i>AIT Austrian Institute of Technology GmbH, Austria</i>



14:00 – 16:00	Afternoon session C2	PCM materials
	Chairperson: Elena Palomo del Bario	
14:00 – 14:20	Nucleation behaviour in organic PCM investigated by microscopy and molecular dynamic simulation <u>Stefanie Tafelmeier</u> <i>ZAE Bayern, Germany</i>	
14:20 – 14:40	Xylitol used as phase change material : nucleation mechanisms of the overcooling rupture by stirring <u>Piquard Louis</u> <i>CEA - LITEN Grenoble, France</i>	
14:40 – 15:00	Electric-field induced crystallization in erythritol <u>Jean-Luc Dauvergne</u> <i>CIC energigUNE, Spain</i>	
15:00 – 15:20	Esters as phase change materials for latent heat storage applications: investigation and control of the polymorphic phases <u>Rebecca Ravotti</u> <i>Lucerne University of Applied Sciences and Arts, Switzerland</i>	
15:20 – 15:40	Validation of lauric acid as PCM: study of thermal degradation under quasi-real working conditions <u>Rocío Bayón</u> <i>CIEMAT-PSA, Spain</i>	
15:40 – 16:00	Compatibility of the novel Cu-67wt.%Mg phase change material in non-inertial thermal storage applications <u>Anthony Rawson</u> <i>German Aerospace Center, Germany</i>	
16:00 – 16:15	Participant networking / Break	
16:15 – 18:48	Short Oral-Poster session	TES applications
	Chairpersons: Gabriel Zsembinszki / Wim van Helden	
16:15 – 16:21	Effect of residual heat recovery of Zeolite Boiler in thermochemical energy storage and transport system <u>Shoma Fujii, University of Tokyo, Japan</u>	
16:22 – 16:28	Numerical analysis of air-PCM compact heat exchangers using rectangular mini-tubes for free cooling in ventilation systems <u>Amir Abdi, KTH Royal Institute of Technology, Sweden</u>	
16:29 – 16:35	Application of macro-encapsulated PCM in light weight building structure for reduction of cooling energy use <u>Eva Zavrl, University of Ljubljana, Slovenia</u>	



16:36 – 16:42	Comparative performance and efficiency analysis of a latent heat storage using HDPE or erythritol for demand-side management <i>Lisa Deinert, Fraunhofer Institute for Environmental, Safety, and Energy Technology, Germany</i>
16:43 – 16:49	Preliminary experimental study of a latent heat thermal energy storage system based on pillow plate technology <i>Ander Rojo Hurtado, Energetic Engineering Department of The UPV/EHU, Spain</i>
16:50 – 16:56	Evaluation of latent heat storage integration in a Swedish multi-family heating system <i>Emma Nyholm Humire, KTH Royal Institute of Technology, Sweden</i>
16:57 – 17:03	Design and optimization of closed-system thermochemical energy storage with surrogate models <i>Gabriele Humbert, University of Birmingham, United Kingdom</i>
17:04 – 17:110	Hybrid storage system to increase self-consumption of buildings <i>Keith O'Donovan, AEE Intec, Austria</i>
17:11– 17:17	Relevance of thermochemical storage in TES field: a bibliometric study <i>A. Inés Fernández, University of Barcelona, Spain</i>
17:18 – 17:30	Questions
17:31 – 17:41	Break
17:42 – 17:48	Numerical analysis of combined heat pump ice energy storage systems to utilize waste heat arising in nonresidential buildings <i>Marco Griesbach, University of Bayreuth, Germany</i>
17:49 – 17:55	Absorption cold storage based on partially crystallized aqueous LiBr-solution <i>Dieter Pressl, ZAE Bayern, Germany</i>
17:56 – 18:02	Development of a sensor for the detection of the charge status of ice storages <i>Stefanie Lott, University of Stuttgart, Germany</i>
18:03 – 18:09	Experimental investigation of zeolite placed in a ventilation duct for space heating <i>Urška Mlakar, University of Ljubljana, Slovenia</i>
18:10 – 18:16	Simulative designing of thermal high performance storages for electric bus heating <i>Werner Kraft, German Aerospace Center, Germany</i>
18:17 – 18:23	Latent thermal energy storage charging and discharging: a numerical study <i>Mateo Kirincic, University of Rijeka, Croatia</i>
18:24 – 18:30	Experimental investigation of latent heat storage integrated on top of wood stoves <i>Alexis Sevault, SINTEF Energy Research, Norway</i>
18:31– 18:37	Impact of transient storage temperature on heat transport system design for a thermal energy storage unit in vehicle applications <i>Frank Nees, German Aerospace Center, Germany</i>
18:38– 18:48	Questions



16:15 – 18:34		Short Oral-Poster session	TES materials
		Chairpersons: Andrea Frazzica / Christoph Rathgeber	
16:15 – 16:21	Reactivity assessment of magnesium chloride and ammonia for thermochemical energy storage	<u>Saki Yoshida</u> , <i>Tokyo Institute of Technology, Japan</i>	
16:22 – 16:28	Experimental performance analysis of a bench-scale NH ₃ -SrCl ₂ thermochemical heat storage system	<u>Saman Nimali Gunasekara</u> , <i>KTH Royal Institute of Technology, Sweden</i>	
16:29 – 16:35	Elaboration and characterization of Li ₄ (OH) ₃ Br-based shape stabilized composites for high temperature thermal energy storage	<u>Imane Mahroug</u> , <i>CIC energiGUNE, Spain</i>	
16:36 – 16:42	Modeling and validation of the dehydration process for thermochemical energy storage using reaction rate equations	<u>Ayeshah Alawadhi</u> , <i>University of Colorado – Boulder, United States</i>	
16:43 – 16:49	Evaluation of ad/desorption dynamics of S-PEEK/Zeolite composite coatings by T-LTJ method	<u>Davide Palamara</u> , <i>University of Messina, Italy</i>	
16:50 – 16:56	Canadian natural zeolites as stable host matrices for low-cost, high-performance composite thermochemical energy storage materials	<u>Dylan Bardy</u> , <i>Natural Resources Canada, Canada</i>	
16:57 – 17:03	Processing salt-hydrates to thermochemical storage composite materials	<u>Gayaneh Issayan</u> , <i>University of Applied Sciences Upper Austria, Austria</i>	
17:04 – 17:10	Tailoring water adsorption capacity of aluminophosphate AlPO ₄ -34	<u>Alenka Ristić</u> , <i>National Institute of Chemistry, Slovenia</i>	
Poster	Thermochemical water-sorption materials screening for thermal energy storage: building application	<u>Anabel Palacios Trujillo</u> , <i>University of Birmingham, United Kingdom</i>	
17:11 – 17:23		Questions	
17:24 – 17:34		Break	
17:35 – 17:41	Preparation of PCL based SS-PCM and shaping using 3D printing	<u>Rebeca Salgado</u> , <i>University of Barcelona, Spain</i>	
17:42 – 17:48	Overview on CSP systems and current advanced technologies used as storage media	<u>Helena Navarro</u> , <i>University of Birmingham, United Kingdom</i>	
17:49 – 17:55	Speed of reaching the full potential heat capacity of a basalt product: mathematical model based on experimental results	<u>Karin Edel</u> , <i>Czech Technical University in Prague, Czech Republic</i>	



17:56 – 18:02	Systematic characterization of various filler configurations for application in molten salt under similar conditions with water <i>Julius Weiss, Fraunhofer Institute for Solar Energy Systems ISE, Germany</i>
18:03 – 18:09	Steel slag concrete: thermo-mechanical stability under high-temperature cycles <i>Laura Boquera, University of Lleida, Spain</i>
18:10 – 18:16	Modeling of combined convective and close-contact melting in a vertical cylindrical enclosure <i>Tomer Shockner, Ben Gurion Universit, Israel</i>
18:17 – 18:23	PCM absorbed exfoliated graphite/polymer composites for thermal management of Lithium-ion batteries <i>Manikantan Kota, Pluss Advanced Technologies Pvt.Ltd, India</i>
18:24 – 18:34	Questions
16:15 – 18:55	Short Oral-Poster session Systems Chairpersons: Ana Lazaro / Rok Stropnik
16:15 – 16:21	Configuration and strategy optimizations for a new distributed energy system combining multi-energy storage techniques <i>Zhijian Liu, North China Electric Power University, China</i>
16:22 – 16:28	An investigation into the use of biomimetic designs for improved efficiency in both solar thermal and solar photovoltaic applications. <i>Adam Lunnon-Collery, Trinity College Dublin, Ireland</i>
16:29 – 16:35	Optimizing Carnot battery configuration for waste heat recovery integrated system with ORC <i>Miroslav Rathan, Czech Technical University in Prague, Czech Republic</i>
16:36 – 16:42	Building stock quantification approach for building retrofit analysis. A case study for PV potential and Energy demand reduction <i>Dieter Boer, Universitat Rovira I Virgili, Spain</i>
16:43 – 16:49	Demand orientated steam generation from phase change material by using a rotating drum heat exchanger <i>Jonas Tombrink, German Aerospace Center, Germany</i>
16:50 – 16:56	Experimental study on the effect of flat and thin slab encapsulation design on a PCM tank <i>David Vérez, University of Lleida, Spain</i>
16:57 – 17:03	Analysis of the behavior of a thermocline tank consists on a packed bed with solid particles <i>Minerva Díaz, Castilla-La Mancha University, Spain</i>
17:04 – 17:10	Low-emission heat supply with heat pumps and hot water storage – Optimal design and operation <i>Dimitri Nefodov, Chemnitz University of Technolgy, Germany</i>



17:11 – 17:17	Use of reinforcement learning to optimize the control of solar thermal collectors coupled to seasonal thermal energy storage <i>Alicia Crespo, University of Lleida, Spain</i>
17:18– 17:30	Questions
17:31 - 17:41	Break
17:42 – 17:48	Effective thermal conductivity from thermal response tests increases with time when sufficient groundwater flow is present <i>Karoline Kvalsvik, Norwegian University of Science and Technology, Norway</i>
17:49 – 17:55	Opportunities for BTES in existing buildings – ideas and first results from project GEO4CIVHIC <i>Burkhard Sanner, UbeG Dr. Mands & Sauer GbR, Germany</i>
17:56 – 18:02	Modeling of the total efficiency of hybrid photovoltaic/thermal collector working in the direct solar energy absorption mode <i>Artem Nikulin, CIC energiGUNE, Spain</i>
18:03 – 18:09	Design and build of a novel dual-tube PCM storage unit <i>Maike Johnson, German Aerospace Center, Germany</i>
18:10 – 18:16	Life cycle assessment of an innovative hybrid energy storage system for residential buildings <i>Noelia Llantoy, University Of Lleida, Spain</i>
18:17 – 18:23	Large-scale cold water storage - German state of the art <i>Thorsten Urbaneck, Chemnitz University of Technology, Germany</i>
18:24 – 18:30	Numerical simulation of a fluidized bed with concentrated radiation directly on SiC particles <i>Minerva Díaz, Castilla-La Mancha University, Spain</i>
18:31 – 18:37	CFD analysis of large scale high temperature thermal energy storage unit <i>Yousif Muhammad, Technical University of Denmark, Denmark</i>
18:38 – 18:44	Different Cycle Layouts for Pumped Thermal Energy Storage (PTES) Systems with Zeotropic Working Fluids <i>Aiko Bernehed, German Aerospace Center, Germany</i>
18:45 – 18:55	Questions
19:05 – 19:50	Welcome / Photo shooting



THURSDAY, 10 JUNE 2021

9:00 – 10:25	Morning session A3 Chairperson: Uroš Stritih	TES applications
9:00 – 9:25	Keynote lecture KL3 Phase change materials: is still the starring technology of thermal energy storage? Current applications, perspectives and research gaps <u>Luisa F. Cabeza</u> <i>University of Lleida, Spain</i>	
9:25 – 9:45	Experimental characterization of two latent heat storage prototypes for domestic heating application <u>Justin Chiu</u> <i>KTH Royal Institute of Technology, Sweden</i>	
9:45 – 10:05	Active PCM-based heat storage using biowax and a pillow-plate heat exchanger in a ZEB building <u>Alexis Sevault</u> <i>SINTEF Energy Research, Norway</i>	
10:05 – 10:25	Thermo-economic analysis of cascaded latent-heat stores in pumped thermal electricity storage systems <u>Yao Zhao</u> <i>Shanghai Jiao Tong University, China</i>	
9:00 – 10:20	Morning session B3 Chairperson: Fabian Ochs	Systems
9:00 – 9:20	Simulations and optimization of BTES systems for commercial and non-residential buildings in project geo base, and validation of BHE simulation <u>Lars Kühl</u> <i>Ostfalia University of Applied Sciences, Germany</i>	
9:20 – 9:40	Methods for the determination of the state-of-charge of a thermal energy storage device <u>Gabriel Zsembinszki</u> <i>University of Lleida, Spain</i>	
9:40 – 10:00	Analysis of the discharging process of latent heat thermal energy storage units by means of normalized power parameters <u>Andreas König-Haagen</u> <i>University of the Basque Country UPV/EHU, Spain</i> <i>University of Bayreuth, Germany</i>	



10:00 – 10:20	Experimental study of AI-based model predictive control strategy for thermal energy storage system <u>Doyun Lee</u> <i>University of Tokyo, Japan</i>
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9:00 – 10:20	Morning session C3	EES materials / applications
	Chairperson: Claudio Gerbaldi	

9:00 – 9:20	Multivalent Batteries and their perspective <u>Robert Dominko</u> <i>National Institute of Chemistry, Slovenia</i>
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9:20 – 9:40	Development of an H₂-permeable, PdCu-based, composite membrane by using a reverse build-up method <u>Yasunari Shinoda</u> <i>Tokyo Institute of Technology, Japan</i>
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9:40 – 10:00	Techno-economic evaluation of Brayton Battery configurations with power-to-heat extension <u>Sergej Belik</u> <i>German Aerospace Center, Germany</i>
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10:00 – 10:20	Ni-doped CdS quantum dots sensitized 3D rosette-rod TiO₂ photoanodes for photoelectrochemical water splitting <u>Gülfeza Kardaş</u> <i>Çukurova University, Turkey</i>
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10:20 – 10:45	Sponsor chat / Break
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10:45 – 12:25	Morning session A4	TES applications
	Chairperson: Luisa F. Cabeza	

10:45 – 11:05	Coupling of building simulation with real time measurements of PCM components - a hardware in the loop approach <u>Stephan Vidi</u> <i>ZAE Bayern, Germany</i>
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11:05 – 11:25	Techno-economic assessment of thermal energy storage systems for small-scale CSP plants running organic Rankine cycles <u>Iñigo Ortega-Fernández</u> <i>CIC energiGUNE, Spain</i>
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11:25 – 11:45	Modeling phase change materials in advanced urban canopy models <u>Claudia Fabiani</u> <i>University of Perugia, Italy</i>
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11:45 – 12:05 **An algorithm for optimal selection of thermal energy storage options in industrial waste heat recovery applications**

Giovanni Manente

University of Birmingham, United Kingdom

12:05 – 12:25 **Giga scale pit storage as an essential part of district heating systems**

Keith O'Donovan

AEE Intec, Austria

10:45 – 12:25 Morning session B4 TCM materials

Chairperson: Stefania Doppiu

10:45 – 11:05 **Experimental study of ettringite materials for thermochemical energy storage in buildings**

Frédéric Kuznik

CETHIL INSA Lyon, France

11:05 – 11:25 **Impact of Fe- and La-doping on the thermochemical heat storage capacity of CaMnO_3**

Emanuela Mastronardo

Institute of Catalysis and Petrochemistry, Spain

University of Messina, Italy

11:25 – 11:45 **Synthetic strategies for the enhancement of tricalcium aluminate hexahydrate hydrothermal cycling performances**

Elpida Piperopoulos

University of Messina, Italy

11:45 – 12:05 **Development of $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ ($0 \leq x \leq 1$) materials for thermochemical energy storage at lower red-ox temperature**

Yasmina Portilla

CIC energiGUNE, Spain

12:05 – 12:25 **Thermochemical storage of low-temperature wasted heat by organic salt hydrate material**

Emanuele La Mazza

University of Messina, Italy

10:45 – 12:25 Morning session C4 Sensible materials

Chairperson: Anna Inés Fernandez

10:45 – 11:05 **Industrial byproducts characterization for high temperature solid particle solar tower systems used as thermal energy storage and heat transfer fluid**

Alejandro Calderón

University of Barcelona, Spain



11:05 – 11:25	The enabling role of nanoparticles in the development of anticorrosion coatings for molten salts thermal energy storage applications <u>Luis González-Fernández</u> <i>CIC energiGUNE, Spain</i>
11:25 – 11:45	High temperature equilibria in molten nitrate salt – Thermal stability in purged and closed systems <u>Alexander Bonk</u> <i>German Aerospace Center, Germany</i>
11:45 – 12:05	Hot corrosion resistance of Inconel 600 under molten salts at 675 °C for thermal energy storage tanks. <u>Adrià Urban</u> <i>University of Barcelona, Spain</i>
12:05 – 12:25	Corrosion study of the use of nitrate molten salt nanofluids in Concentrated Solar Plants <u>Helena Navarro</u> <i>University of Birmingham, United Kingdom</i>
12:25 – 14:00	Sponsor chat / Break
14:00 – 15:40	Afternoon session A5 Chairperson: Teun Bokhoven Climate
14:00 – 14:20	Analyzing online news to understand thermal energy storage awareness and acceptance <u>Claudia Fabiani</u> <i>University of Perugia, Italy</i>
14:20 – 14:40	Analysis of electricity consumption in Slovenia until 2050 by integrating RES with the role of energy storage technologies <u>Uroš Stritih</u> <i>University of Ljubljana, Slovenia</i>
14:40 – 15:00	A techno-economic analysis of compact thermal energy storage technology: energy & cost savings, load-shifting potential, and 2030 cost targets <u>Dylan Bardy</u> <i>Natural Resources Canada, Canada</i>
15:00 – 15:20	The influence of distinctive urban morphologies on the microclimate in Singapore <u>Luisa F. Cabeza</u> <i>University of Lleida, Spain</i>
15:20 – 15:40	Role of onsite thermal and electric storage in nZEBs <u>Fabian Ochs</u> <i>University of Innsbruck, Austria</i>



14:00 – 15:45	Afternoon session B5 Chairperson: Camila Barreneche	PCM materials
14:00 – 14:25	Keynote lecture KL4 Trends in PCM development – From CalorSTOCK'94 to EnerSTOCK'21 <u>Halime Paksoy</u> <i>Çukurova University, Turkey</i>	
14:25 – 14:45	Effect of the processing method in trimethylolethane based composites for thermal energy storage systems <u>Ángel Serrano</u> <i>CIC energiGUNE, Spain</i>	
14:45 – 15:05	Parametric characterization of the variables that influence supercooling on PCMs <u>Laura Quant Colón</u> <i>University of the Basque Country UPV/EHU, Spain</i>	
15:05 – 15:25	Thermal characterisation of the novel Cu-67 wt. % Mg phase change material for thermal storage applications <u>Carolina Villada Vargas</u> <i>German Aerospace Center, Germany</i>	
15:25 – 15:45	Testing the use of UA-values for comparison of two different PCM-heat exchanger <u>Dominic Groulx</u> <i>Dalhousie University, Canada</i>	
14:00 – 15:40	Afternoon session C5 Chairperson: Christoph Zauner	TES applications
14:00 – 14:20	Parametric study of the PCM system for space cooling improved with the night-time ventilation for the enhanced solidification <u>Eva Zavrl</u> <i>University of Ljubljana, Slovenia</i>	
14:20 – 14:40	Promotion of thermal comfort thanks to PCM: also still after 10 years of operation? <u>Tabea Oberfell</u> <i>Fraunhofer Institute for Solar Energy Systems ISE, Germany</i>	
14:40 – 15:00	Thermal analysis and simulation of solar building heating systems utilizing heat pumps and phase change energy storage <u>José A. Almendros-Ibáñez</u> <i>Castilla-la Mancha University, Spain</i>	
15:00 – 15:20	Techno-economic evaluation of nitrate salt storage concepts at 620 °C <u>Freerk Klasing</u> <i>German Aerospace Center, Germany</i>	



15:20 – 15:40	Experimental comparison of small-scale and full-scale latent storage for integration in efficient heat pumps <u>Gabriel Zsembinski</u> <i>University of Lleida, Spain</i>
15:40 – 16:15	Participant networking / Break
16:15 – 18:39	Short Oral-Poster session TES applications Chairpersons: Gonzalo Diarce Beloso / Eneja Osterman
16:15 – 16:21	ASTEP project: development of high temperature thermal energy storage systems for industrial processes <u>Juan Enríquez</u> , <i>Polytechnic University of Cartagena, Spain</i>
16:22 – 16:28	Groundwater influence on large-scale hot water tanks and pits for renewables-based district heating systems: technical assessment <u>Abdulrahman Dahash</u> , <i>University of Innsbruck, Austria</i>
16:29 – 16:35	Experimental analysis of a small size vacuum insulated water tank <u>Emiliano Borri</u> , <i>University of Lleida, Spain</i>
16:36 – 16:42	Experimental evaluation of a heat pump-latent storage system for increasing renewable share of the residential stock <u>Valeria Palomba</u> , <i>CNR ITAE, Italy</i>
16:43 – 16:49	Review of thermal energy storage in heat pump systems for heating and cooling <u>Eneja Osterman</u> , <i>University of Ljubljana, Slovenia</i>
16:50 – 16:56	Modelling very large thermal energy stores - comprehensive comparison of different models <u>Fabian Ochs</u> , <i>University of Innsbruck, Austria</i>
16:57 – 17:03	Radial diffusers with twist generation for arrow storage tanks – first experimental studies <u>Thorsten Urbaneck</u> , <i>Chemnitz University of Technology, Germany</i>
17:04 – 17:10	Economic optimization of seasonal thermal energy storage systems <u>Reto Hendry</u> , <i>Lucerne University of Applied Sciences and Arts, Switzerland</i>
Poster	Building a predictive model for a heat source system with thermal energy storage using machine learning <u>Yuki Matsuda</u> , <i>DAI-DAN Co., Ltd., Japan</i>
17:11 – 17:21	Questions
17:22 – 17:32	Break
17:33 – 17:39	Temperature distribution on directly irradiated spouted beds <u>José A. Almendros-Ibáñez</u> , <i>Castilla-la Mancha University, Spain</i>



17:40 – 17:46	Business case improvement of a multi-energy plant containing a wood boiler, an organic Rankine cycle and two thermal energy storage vessels <i>Jad Al Koussa, Vito/EnergyVille, Belgium</i>
17:47 – 17:53	A study of spacing effect on pool boiling performance of three triangular pitched and vertically oriented tubes <i>Artem Nikulin, CIC energiGUNE, Spain</i>
17:54 – 18:00	Validation of numerical model for latent thermal storage operation and analysis of heat charge and discharge in TRNSYS <i>Rok Koželj, University of Ljubljana, Slovenia</i>
18:01 – 18:07	Development and analysis of a CFD results based system simulation model for a latent heat thermal energy storage unit with macro-capsules <i>Andreas König-Haagen, University of the Basque Country UPV/EHU, Spain, University of Bayreuth, Germany</i>
18:08 – 18:14	Experimental study of a novel three-fluids heat exchanger embedded with phase change materials for cooling applications <i>Boniface Dominick Mselle, University of Lleida, Spain</i>
18:15 – 18:21	Long term performance evaluation of large scale ATEs for commercial buildings: case study in Stockholm <i>Mohammad Abuasbeh, KTH Royal Institute of Technology, Sweden</i>
18:22 – 18:28	Chemical impacts of shallow aquifer thermal energy storage: statistical analysis for first year of operation of study case in Sweden <i>Mohammad Abuasbeh, KTH Royal Institute of Technology, Sweden</i>
18:29 – 18:39	Questions
16:15 – 18:55	Short Oral-Poster session PCM materials Chairpersons: Harald Mehling / Dominic Groulx
16:15 – 16:21	Formation mechanism of Al@Al₂O₃ core-shell type microencapsulated phase change material <i>Yuto Shimizu, Hokkaido University, Japan</i>
16:22 – 16:28	Onset of natural convection during PCM melting <i>Dominic Groulx, Dalhousie University, Canada</i>
16:29 – 16:35	Characterization of two phase change materials for domestic hot water application <i>Laurent Zalewski, Artois University, France</i>
16:36 – 16:42	Synthesis of microcapsulated of PCMs with natural shell materials prepared according to green chemistry principles <i>Sedat Emir, Çukurova University, Turkey</i>
16:43 – 16:49	Thermal contact resistance: implications for thermal energy storage systems <i>Veronika Stahl, German Aerospace Center, Germany</i>



16:50 – 16:56	Development of a prototype to research on xylitol crystallization by shearing and seeding for its use as a phase change material <i>Miguel Navarro, University of Zaragoza, Spain</i>
16:57 – 17:03	Possibilities and limitations of PCM development using phase diagrams <i>Christoph Rathgeber, ZAE Bayern, Germany</i>
17:04 – 17:10	Shape-stabilized phase change materials obtained by single screw extruder for building applications: thermo-physical characterization <i>Rebeca Salgado, University of Barcelona, Spain</i>
17:11 – 17:17	Sensitivity analysis of examination methods to determine the degradation of erythritol and HD-PE <i>Franziska Klünder, Fraunhofer Institut For Solar Energy Systems ISE, Germany</i>
17:18– 17:30	Questions
17:31 - 17:41	Break
17:42 – 17:48	Developing PCM-PVA gel composite bio-inspired by whale blubber for TES <i>Özge Güngör, Çukurova University, Turkey</i>
17:49 – 17:55	Reduction of rotation phase supercooling in nano n-docosanol phase change slurries <i>Moritz Kick, Fraunhofer Institute for Solar Energy Systems ISE, Germany</i>
17:56 – 18:02	Stability of latent heat storage units: evaluation based on the compatibility tests <i>Milan Ostrý, Brno University of Technology, Czech Republic</i>
18:03 – 18:09	Own synthesize nano-enhanced fatty acid phase change materials (NEPCM): a comparison of properties <i>Marc Majo, University of Barcelona, Spain</i>
18:10 – 18:16	Measuring crystallisation rates of phase change materials as a function of supercooling <i>Stefanie Tafelmeier, ZAE Bayern, Germany</i>
18:17 – 18:23	Development of microencapsulated phase change materials suitable for fluidized bed thermal energy storage systems <i>Gizem Biçer Göktepe, Çukurova University, Turkey</i>
18:24 – 18:30	Thermal characterization of a latent heat thermal energy storage system through an 8.5 kWh experimental prototype <i>Raffaele Liberatore, ENEA, Italy</i>
18:31 – 18:37	Measuring thermophysical properties for an open-source PCM library <i>Lukas Müller, Lucerne University of Applied Sciences and Arts, Switzerland</i>
18:38 – 18:44	A review on phase change materials, utilization in the aeronautical field <i>Christos Potamitis, University of West Attica, Greece</i>
18:45 – 18:55	Questions
19:05 – 19:35	Photo shooting



FRIDAY, 11 JUNE 2021

9:00 – 10:25	Plenary Session P2 Chairperson: Uroš Stritih	
9:00 – 9:45	Plenary lecture PL2 100% Renewable smart energy systems <u>Henrik Lund</u> <i>Aalborg University, Denmark</i>	
	Short break	
9:50 – 10:30	Morning session A6 Chairperson: Yaroslav Grosu	TES applications
9:50 – 10:10	Carnot-batteries and the decarbonization of coal fired power plants <u>Andre Thess</u> <i>German Aerospace Center, Germany</i>	
10:10 – 10:30	Demonstration of two latent heat storages for industrial solar process heat applications <u>Christoph Zauner</u> <i>AIT Austrian Institute of Technology, Austria</i>	
9:50 – 10:30	Morning session B6 Chairperson: Rafeale Liberatore	P2X applications
9:50 – 10:10	District cooling system optimization with distributed cold storage adopting power-to-cold: a case study on Norrenergi AB <u>Saman Nimali Gunasekara</u> <i>KTH Royal Institute of Technology, Sweden</i>	
10:10 – 10:30	Flexibility of refrigeration systems for grid balancing in Germany <u>Dana Laureen Schmidt</u> <i>Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT, Germany</i>	
9:50 – 10:30	Morning session C6 Chairperson: Helena Navarro	Sensible materials
9:50 – 10:10	Chemisorption at solid-liquid interfaces as a mechanism for enhanced sensible energy storage in nanofluids <u>Ivan Carrillo-Berdugo</u> <i>University of Cadiz, Spain</i>	



10:10 – 10:30	Nanofluids study through infrared thermography and physico-chemical characterization <u>Adela Svobodova Sedlackova</u> <i>University of Barcelona, Spain</i>
10:30 – 10:45	Participant networking / Break
10:45 – 12:25	Morning session A7 TES applications Chairperson: Andre Thess
10:45 – 11:05	Commissioning of high temperature thermal energy storage for high power levels <u>Maike Johnson</u> <i>German Aerospace Center, Germany</i>
11:05 – 11:25	Enhancing energy density of existing sensible thermal storage system with encapsulated PCM <u>Rok Koželj</u> <i>University of Ljubljana, Slovenia</i>
11:25 – 11:45	Effect of fluid velocity on storage performance of medium temperature packed-bed thermal energy storage systems <u>Burcu Koçak</u> <i>Çukurova University, Turkey</i>
11:45 – 12:05	Thermal high performance storages for electric bus heating - overview on the current state of development <u>Werner Kraft</u> <i>German Aerospace Center, Germany</i>
12:05 – 12:25	An insight into challenges associate with seasonal storage in solar district heating systems <u>Mohamed Abokersh</u> <i>University of Rovira i Virgili, Spain</i>
10:45 – 12:25	Morning session B7 PCM materials Chairperson: Halime Paksoy
10:45 – 11:05	Hybridisation of latent and thermochemical thermal energy storage: 3 in 1 thermal energy storage <u>Anabel Palacios Trujillo</u> <i>University of Birmingham, United Kingdom</i>
11:05 – 11:25	Synthesis and characterization of microcapsules based on inorganic@PCM for thermal energy storage at low temperature applications <u>Teresa Aguilar</u> <i>University of Cadiz, Spain</i>



11:25 – 11:45	Hierarchical macro-nanoporous metals for shape-stabilized phase change materials with high energy capacity, enhanced thermal conductivity and superior antileakage performance <u>Yaroslav Grosu</u> <i>CIC energiGUNE, Spain</i>
11:45 – 12:05	Evaluation of nitrate salts as storage medium for active latent heat thermal energy storage systems <u>Andrea Gutierrez</u> <i>German Aerospace Center, Germany</i>
12:05 – 12:25	Effect of adding expanded graphite microparticles in organic plastic crystals for latent heat storage <u>Sergio Santos-Moreno</u> <i>CIC energiGUNE, Spain</i>
10:45 – 12:25	Morning session C7 Chairperson: Frédéric Kuznik Systems
10:45 – 11:05	Use of a simplified numerical model for the thermal performance evaluation of a tube&shell LHTES <u>Daniele Nicolini</u> <i>ENEA, Italy</i>
11:05 – 11:25	Life Cycle Assessment (LCA) of concentrating solar power (CSP) plant in tower configuration with and without thermal energy storage (TES) <u>Gemma Gasa</u> <i>University of Lleida, Spain</i>
11:25 – 11:45	Impact of PEMFC performance and durability on life cycle environmental impacts <u>Rok Stropnik</u> <i>University of Ljubljana, Slovenia</i>
11:45 – 12:05	Analyzing Different Thermal Management Systems for Li-ion battery pack - CFD Study <u>Yousif Muhammad</u> <i>Technical University of Denmark, Denmark</i>
12:05 – 12:25	Multi-scale modelling of the thermal runaway in Li-ion batteries <u>Tomaž Katrašnik</u> <i>University of Ljubljana, Slovenia</i>
12:30 – 14.00	Participant networking / Break



14:00 – 15:00	Afternoon session A8	TES applications
	Chairperson: Masaya Okumiya	
14:00 – 14:20	Applications of thermal energy storage systems for nearly-zero energy demonstration buildings in China <u>Xinyan Yang</u> <i>China Academy Of Building Research, China</i>	
14:20 – 14:40	Development and demonstration of a Zero-Energy-Sauna <u>Micha Schaefer</u> <i>University of Stuttgart, Germany</i>	
14:40 – 15:00	Developing northern greenhouses : an experimental and numerical studies <u>Didier Hailot</u> <i>Ecole De Technologie Supérieure, Canada</i>	
14:00 – 15:05	Afternoon session B8	P2X/TCM materials
	Chairperson: Luigi Calabrese	
14:00 – 14:25	Keynote lecture KL5 Photocatalytic CO₂ and CH₄ conversion to H₂ and CO beyond thermodynamic equilibrium for a possible power to gas application <u>Petar Djinoić</u> <i>National Institute of Chemistry, Slovenia</i>	
14:25 – 14:45	Thermochemical heat storage through CaO-Mayenite/CaCO₃ system: thermal performances comparison for two synthesis methods. <u>Raffaele Liberatore</u> <i>ENEA, Italy</i>	
14:45 – 15:05	Cyclic CO₂ hydrate-based cold thermal storage and CO₂ gas storage enabled by amine infused hydrogels <u>Xiaolin Wang</u> <i>The Australian National University, Australia</i>	
14:00 – 15:00	Afternoon session C8	PCM materials
	Chairperson: Rocio Bayón	
14:00 – 14:20	Valorization of red mud as a supporting material for medium-high temperature thermal energy storage <u>Argyrios Anagnostopoulos</u> <i>University of Birmingham, United Kingdom</i>	
14:20 – 14:40	Potential new reference materials for caloric measurements on PCM <u>Harald Mehling</u> <i>Consultant, Germany</i>	
15:10 – 15:30	EERA JP ES, Salvatore Vasta, Coordinator of the EERA Sub-Program on TES Awards and closing	



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PRIKLOPLJENI NA POZITIVNO ENERGIJO

Verjamemo v svetlo energetska prihodnost. Kot največji slovenski proizvajalec in prodajalec električne energije iz lastnih, domačih virov s pozitivnostjo sprejemamo odgovornost trajnostnega energetskega prehoda v Sloveniji. Naše elektrarne že zdaj proizvedejo več kot tri četrtine vse električne energije iz obnovljivih virov. Kot osrednji steber slovenskega elektroenergetskega sistema zagotavljamo stabilno in zanesljivo oskrbo. Naše delovanje in razvoj temeljita na načelu odgovornosti do okolja in družbe. Z izkušnjami in znanjem več kot tri tisoč strokovnjakov v skupini HSE odpiramo nove razvojne priložnosti, ob stalnem nadgrajevanju strateških partnerstev tako doma kot v tujini pa utiramo pot v zanesljivo prihodnost proizvodnje električne energije.





ABSTRACTS

ENERSTOCK 2021

OPENING

PAST, PRESENT AND FUTURE WORK IN IEA ENERGY STORAGE TCP

Teun Bokhoven¹

¹*Energy Storage TCP, Moordrecht, Netherlands*

Article presents the priority areas for research on energy storage technologies under the auspices of Energy Storage TCP:

- System integration: Energy storage enabling flexibility and sector coupling, including bi-directional applications and focus on more integrated system packages
- Electrical Storage: focus on system aspects of electrical storage and new and innovative storage concepts
- Thermal Storage: focus on thermo-chemical / thermo-physical, Phase Change Materials (PCM), sensible thermal storage (at all temperatures ranges and serving various applications)/
- Hybrid Options: focus on power to heat (P2H), power to gas (P2G- within boundaries of gas/H₂ as energy storage and carrier/vector serving system integration) and specific conversion technologies, efficiencies, etc

IEA Technology Network and TCP structure will be explained with special focus on Energy Storage TCP. A growing scientific and political interest in energy storage is evident. This is recently illustrated by the EC's proposed recovery strategy where energy storage is an explicit and prominent part. International organizations play an increasingly important role in deploying and disseminating information on energy storage and the effects of Covid-19 may influence the speed of the energy transition. All this drives the need for more and improved storage solutions. The ES TCP contributes through international collaboration to this need by further research, development and effective deployment of energy storage. These considerations are the basis for the ES TCP's Mission: Energy Storage contributes and provides solutions for the challenge to tackle climate change and the transformation to a circular economy.

Based on this mission, the activities of Energy Storage TCP relate to integral research, development, implementation and integration of energy-storage technologies to optimize the energy efficiency of all kinds of energy system and to enable the increasing use of renewable energy instead of fossil fuels. To use the expertise and experience efficiently and gain benefits from the resulting synergies, high-level coordination is needed to develop suitable working plans and research goals. ES TCP strategic plan therefore includes research activities (strategies for scientific research and development, dissemination and market deployment), as well as co-ordination activities.

Finished, present and future annexes will also be presented and explained.

ENERSTOCK 2021

TOWARDS SUSTAINABLE ENERGY SOCIETY IN SLOVENIA

Uroš Stritih¹, Alenka Ristić²

¹*Faculty of Mechanical Engineering, University of Ljubljana, Slovenia*

²*National Institute of Chemistry, Ljubljana, Slovenia*

INTRODUCTION: Slovenia became in 2012 a member of IEA ECES (apart from Belgium, Canada, China, Denmark, Finland, France, Germany, Italy, Japan, Korea, the Netherlands, Norway, Sweden, Turkey, Spain, Poland and the United States) following the decision of the Government of the Republic of Slovenia. Formally, the cooperation agreement was signed by the University of Ljubljana - Faculty of Mechanical Engineering. Uroš Stritih is a Slovenian delegate, while Alenka Ristić became an alternative delegate last year (replacing retired prof. V. Butala).

RESULTS: In the context of the Annex 21 and Annex 27 a TRT test (Thermal Response Test) was designed and manufactured at the Laboratory for heating, sanitary and solar technology and air-conditioning from the University of Ljubljana - Faculty of Mechanical Engineering. The experimental apparatus was made and experimentally used in boreholes. It is meant to be used in combination with a heat pump.

Faculty of Mechanical Engineering has been involved in a project entitled: Forecast of development of the acquisition of electricity transmission network of the Republic of Slovenia till 2050 whose carrier was ELES (Slovenian Electricity Transmission System Operator). In the framework of this task ELES showed interest in the results of the Annex 26 and in participation in Annex 28 in this field. In December 2013 a kick off meeting for Annex 31 entitled Energy storage within Energy Efficient Buildings was held. In this annex Laboratory for heating, sanitary and solar technology and air-conditioning actively participated. Now a new Annex 37 with a title of Smart design and control of energy storage systems is prepared where UL-FME is participating.

Alenka Ristić works at Department of Inorganic Chemistry and Technology at the National Institute of Chemistry. Her expertise is designing new TCM materials, specifically porous water adsorbents and composites for low temperature sorption heat storage. She has been involved as a subtask leader of the working group on development of compact TES materials in the IEA joint SHC/ECES Tasks/Annexes: Annex 29 "Compact Thermal Energy Storage" (2013-2015) and Annex 33 »Material and Component development for Thermal Energy Storage« (2017-2019). She also participated in the Annex 24 »Compact Thermal Energy Storage: Material Development for System Integration« (2009-2012). In the scope of Annexes 29 and 33 she hosted two experts meetings at National Institute of Chemistry in Ljubljana. Now she is participating in the Annex 35 »Flexible Sector Coupling«.

CONCLUSION: New Annexes are under development. Namely, Annex 37 with a title of Smart design and control of energy storage systems, where UL-FME will be participating. While National Institute of Chemistry) will take part in a new Annex on PCM and TCM materials development in the next year.

ENERSTOCK 2021

PLENARY LECTURES

WHAT IS THE VALUE OF ENERGY STORAGE?

Andreas Hauer

¹ZAE Bayern, Garching, Germany

Energy storage is not for free and provides (in most cases) efficiencies lower than 100 %. That means there have to be benefits of energy storage implementation in a certain application compensating this. Important in this context is the strong dependence on actual applications or in our wording the actual “storage configuration” - consisting of an energy source, the storage itself and finally the consumer.

In general the benefit of an energy storage configuration is the availability of energy (and power) at certain times. The value of energy storage can be quantified by how much somebody is willing to pay for this benefit. And finally, for developing a business case, it has to be identified, who would pay for this.

These questions will be addressed, covering all energy storage technologies and all fields of application. A number of existing examples of successful energy storage implementation will illustrate the approach.

100% RENEWABLE SMART ENERGY SYSTEMS

Henrik Lund¹

¹*Aalborg University, Aalborg, Denmark*

This presentation elaborates on the concept of Smart Energy Systems and presents a case of applying such a concept to the design of a 100% renewable energy future for a local community in Europe by 2050. Aalborg in Denmark is used as a case and the study focuses on how such a local community is to be seen as part of the Danish as well as the European overall strategies.

In recent years, the terms “Smart Energy” and “Smart Energy Systems” have been used to express an approach that reaches broader than the term “Smart grid”. Where Smart Grids focus primarily on the electricity sector, Smart Energy Systems take an integrated holistic focus on the inclusion of more sectors (electricity, heating, cooling, industry, buildings and transportation) and allows for the identification of more achievable and affordable solutions to the transformation into future renewable and sustainable energy solutions.

It is often highlighted how the transition to renewable energy supply calls for significant electricity storage. However, one has to move beyond the electricity-only focus and take a holistic energy system view to identify optimal solutions for integrating renewable energy. In this presentation, an integrated cross-sector approach is used to argue the most efficient and least-cost storage options for the entire renewable energy system concluding that the best storage solutions cannot be found through analyses focusing on the individual sub-sectors. Moreover, such an approach leads to solutions primarily based on existing energy infrastructures rather than leading to significant extra investments.

The presentation presents a set of methods and criteria to design Smart Energy Cities, while taking into account the context of 100% renewable energy on a national level. Cities and municipalities should handle locally what concerns local demands, but acknowledge the national context when discussing resources and industrial and transport demands. To illustrate the method, it is applied to the case of transitioning the municipality of Aalborg to a 100% renewable Smart Energy System within the context of a Danish and European energy system.

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KEYNOTE LECTURES

THERMAL ENERGY STORAGE: DEVELOPMENTS AND RESULTS FOR LARGE SCALE TECHNOLOGIES AND FOR COMPACT TECHNOLOGIES

Wim van Helden¹, Maria Moser², Christoph Muser³, Gernot Wallner⁴, Fabian Ochs⁵, Ingo Leusbrock¹, Daniel Lager⁶, Alenka Ristić⁷, Stefan Gschwander⁸, Christoph Rathgeber⁹, Ana Lazaro¹⁰, Benjamin Fumey¹¹, Andreas Hauer⁹

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⁴Johannes Kepler University Linz, Linz, Austria,

⁵University of Innsbruck, , Austria,

⁶Austrian Institute of Technology, Vienna, Austria,

⁷National Institute of Chemistry, Ljubljana, Slovenia,

⁸Fraunhofer Institute for Solar Energy, Freiburg, Germany,

⁹ZAE Bavarian Centre for Applied Energy, Garching, Germany,

¹⁰University of Zaragoza, Spain,

¹¹EMPA, Dübendorf, Switzerland

Thermal energy storage (TES) technologies play an enabling role in further integrating renewable heat sources in the energy system, from domestic applications through district heating (DH) and industrial applications to the power sector. Furthermore, they provide the necessary flexibility for the coupling of energy sectors. Integration of TES into DH systems calls for larger water-based TES, with a number of specific design requirements imposed by ground structure, large structure building aspects and DH integration. In the first part of this presentation, the developments of very large TES for integration into DH will be highlighted.

On the other hand, when higher temperatures, volume restrictions, or very long storage periods come into play, new compact TES are needed. These technologies need further development to be applicable in the different energy sectors, being the motivation for the IEA SHC Task58/ES Annex33: Material and Component Development for Thermal Energy Storage – to further improve the storage materials and components based on a better knowledge of the underlying physics and chemistry. The activities in this IEA collaboration will be highlighted in the second part.

Developments and results for large scale TES

To reach the long-term goal of 100% renewable energy supply, DH networks require large-scale TES technologies with volumes that are significantly higher than those presently in operation of about 100,000 m³. High urban land price leads to preferably deeper pits, needing dedicated construction techniques.

Experience with the existing plants is still limited due to the low number and young age of the storages. Cost effectiveness and system integration call for higher storage density and thus higher temperatures. This, the higher volume and the additional requirements of vapor tightness, serviceability and durability of innovative solutions for lid, wall and liners call for novel materials and components as well as for improved durability testing methods.

The project giga_TES is a three-year Austrian flagship project targeting at the development of large-scale thermal storage concepts for renewable districts, with a focus on feasible Austrian implementations. The consortium consists of key material and component industries, a major construction company, an engineering and two DH companies, backed by four Austrian and two foreign research institutes that have good knowledge on large thermal energy storages.

ENERSTOCK 2021

Keynote lectures

The project takes the DH networks of Vienna and Salzburg to define a set of application scenarios. The soil composition, including ground water depth and flow, and the integration into the district heating network are the main determining boundary conditions for the thermal energy storage design.

Accelerated ageing tests are used to assess the endurance of newly developed polymer materials that have higher lifetime, are more temperature resistant and have high vapor tightness. A very important outcome is that the family of polypropylenes shows a doubling of the expected lifetime compared to the present standard.

The storage wall consists of a number of layers that together provide strength, water and water vapor tightness and thermal insulation. Three specific volumes of 100.000, 500.000 and 2.000.000 m³ are studied, with a geometry either shaft-like, with vertical walls or pit-like, with sloped walls, or a combination of the two.

Special attention was given to the design of the lid, as this has to enable the use of the storage surface in order to have a better profitability of the storage. Both floating and self-carrying lid concepts have been developed, and the modular, floating lid solution led to a patent application. A number of known problems like the drainage of rain water from the lid, the formation of air pockets underneath the lid and the durability of the thermal insulation were tackled in the novel concepts.

Different simulation environments were set up: for the interaction of the storage with the ground and ground water, for the hydraulics in the storage and for the energy performance of storage in combination with the DH system. With these, the performance of the different wall geometries and materials were investigated, and the influence of the soil with and without groundwater flow investigated. This led to a choice for a construction with inner wall for the water containment and an outer wall serving as groundwater barrier. The dry soil between the two walls serves as thermal insulation, provided that the moisture level is kept low. Experiments with mock-ups of a novel soil-based insulation layer are being performed since spring 2020 and gave satisfying results.

Developments and results for compact TES

The SHC/ES Task58/Annex33 work was mainly concentrated on the fields of materials development and characterisation, on testing methods under application conditions and on component design.

In the class of thermochemical materials (TCM) novel combinations of porous carrier materials and active sorption or hydration materials were developed, with improved performance characteristics. For phase change materials, work was focused on improving methods to determine material characteristics, like thermal conductivity or viscosity.

In order to be able to optimise a compact TES system, the performance of a storage material in a component should be determined properly. This calls for measurement methods under realistic application conditions. For PCM, long-term stability is an important characteristic, and as a first step the different measurement devices and methods have been identified and described.

In order to define reliable and replicable test methods for TCM, round-robin tests for both sorption and hydration materials have been designed and performed. For sorption, this led to satisfying results, while for the hydrate more tests are needed to better understand the influence of the different factors.

Storage component design optimisation is difficult both for PCM and TCM. As a basis, a normalised power versus time PCM performance was designed, enabling comparison of very different designs. For TCM, a system classification method was set up, enabling a systematic description of the components and their dependent and independent parameters.

AN OVERVIEW ON HYBRID POLYMER ELECTROLYTES FOR NEXT-GEN SOLID-STATE BATTERIES OPERATING AT AMBIENT TEMPERATURE

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INTRODUCTION: Standard commercial batteries use liquid electrolytes as ion transport media; these are based on toxic and volatile organic carbonate solvents, and their flammability clearly raises safety concerns. The most striking solution at present is to switch on all solid-state designs exploiting polymer materials, films, ceramics, etc. [1] Polymer electrolytes are proposed as a safe alternative and, particularly in lithium-ion battery (LiB) sector, the transformation from liquid-state to solid-state construction is expected to improve safety, fast and reliable fabrication, and temperature stability. However, several constraints have impeded their intrusion into the mainstream such as low ionic conductivity, low cation transport properties and stringent processing conditions (use of organic solvents). Thus, researchers worldwide have proposed several approaches including the most promising in situ preparation of thermoset polymer electrolytes using the well-established solvent-free processes. Ionic conductivity can be controlled by reducing the crystallinity, which in turn increases the amorphous character of the polymer matrix. Indeed, lithium ion conduction is directly linked to polymer chain mobility. Several approaches have been adopted to reduce the crystalline behaviour of the polymer matrix such as addition of plasticisers, ceramic fillers and proper crosslinking, which are here overview with practical examples from results obtained in our laboratories.

RESULTS: In the first part of the talk, an overview will be offered of the recent developments on innovative polymer electrolytes for alkali metal, particularly Li- and Na-based batteries. In our Labs, we develop different kind of polymer electrolytes by means of different techniques, including simple solvent casting and free radical UV-induced photopolymerization (UV-curing) [2,3]. UV-curing takes place at RT: a liquid poly-functional monomer, containing a proper photo-initiator, forms a cross-linked film upon UV irradiation. It appears highly advantageous, due to its easiness and rapidity in processing, very short time with high efficiency and eco-friendliness as the use of solvent is avoided, thus easily scalable to an industrial level. All samples are thoroughly characterized in the physico-chemical and electrochemical viewpoint. They exhibit excellent ionic conductivity and wide electrochemical stability window, which ensure safe operation even at ambient conditions. Electrochemical performances in lab-scale devices are improved by the use of different kind of RTILs or other specific additives and evaluated by means of cyclic voltammetry and galvanostatic charge/discharge cycling exploiting different electrode materials (eventually prepared by water-based procedures exploiting green carboxymethylcellulose as binder) as well as direct polymerization procedures on top of the electrode films in order to obtain an intimate electrode/electrolyte interface and a full active material utilization [3,4].

Nowadays, possible concerns about the safety of rechargeable lithium metal batteries has postponed their introduction into the smart electronics or automotive industries and have promoted advances in the field of non-flammable solid electrolytes. Among the oxide ceramic super lithium ion conductors, garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) has recently attracted much attention because of its relatively high ionic conductivity at room temperature (approaching 10^{-3} S/cm), negligible electronic conductivity and absence of harmful decomposition products upon contact with atmospheric moisture. Anyway, processing LLZO in pellets by sintering, results in brittle and more or less porous electrolytes, which often display poor interfacial contact

with Li metal electrodes. To circumvent these problems, recent efforts have been dedicated to the formulation of new NASICON-type structures with LAGP and/or LAGTP following new glass-ceramic synthesis routes. As a result, composite hybrid polymer electrolytes (CPEs), where the ceramic material is embedded in a polymeric matrix, are prepared. As compared to the pristine components, CPEs are stiff while preserving flexibility, are easily processed, and can be conceived to attain improved ionic conductivity and interfacial contact with the electrodes [4].

As a result, in the second part of the talk, the results will be given about the development of a polymer based matrix containing poly(ethylene oxide) (PEO), lithium bis (trifluoromethylsulphonyl)imide (LiTFSI), tetra(ethylene glycol dimethyl ether) (G4) and a photoinitiator, which was added with LLZO particles, thoroughly mixed, formed into a film and cross-linked under UV radiation to obtain a composite hybrid electrolyte [4]. Overall, crosslinking allows obtaining self-standing CPEs with desirable properties of flexibility, shape retention upon thermal stress, improved interfacial contact with the metal electrodes and ionic conductivity suitable for practical application. Lab-scale Li-/Na-metal cells as well as Li-/Na-ion full cells assembled with both lithium iron phosphate (LFP) and high-voltage NMC or NaVPF cathodes demonstrated specific capacities approaching 150 mAh/g at 0.1 mA/cm² and could work for hundreds of cycles at ambient temperature [3-5].

CONCLUSION: A multidisciplinary approach is adopted in our Labs to understand the role of photopolymerisation in tailor making the integral and requisite properties of the resulting polymer electrolyte to achieve acceptable conductivity, ionic mobility and resilience towards dendrite-induced short circuit reactions. Significantly, the feasibility of using novel electrolytes in real cell configuration at ambient temperature with various nanostructured electrodes is established by suitably adopting in situ polymerization directly over the electrode films, leading to the assembly of superior Li-/Na-ion and Li-/Na-metal cells conceived for applications that demand high energy and/or power, including smart-grid storage and electric-/hybrid-electric vehicles. We anticipate that the proposed approach would lead to a rational designing to address the significant challenges of alkali metal ion polymer batteries.

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PHASE CHANGE MATERIALS: IS STILL THE STARRING TECHNOLOGY OF THERMAL ENERGY STORAGE? CURRENT APPLICATIONS, PERSPECTIVES AND RESEARCH GAPS

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ABSTRACT

The importance of reducing carbon emission to the atmosphere has led to a radical transition of the energy sector encouraging policymakers to look forward to energy management strategies to reduce energy consumption and increase the share of energy produced by clean sustainable sources. When thermal energy is involved, storing energy through thermal energy storage (TES) is important to both overcome the issue of intermittency of renewables and to increase the efficiency of energy systems. Amongst all the TES, latent heat TES has been the silver bullet of thermal energy storage technologies for the last 20 years. This type of storage relies on the use of phase change materials, which are particularly attractive due to their high energy density and the ability to store thermal energy at nearly isothermal temperature. Furthermore, the large variety of PCMs makes latent heat TES suitable for different applications in a wide temperature range. The number of publications related to latent heat TES started to gain momentum in the literature around the year 2008 and nowadays the trend is still increasing attracting year by year the attention of more researchers. Today, the research community is putting a lot of effort into the development of new materials as well as the innovative applications of PCM. Indeed, although for many years buildings and solar applications were the most common applications studied, applications such as cryogenics, waste heat recovery, geothermal, and refrigeration systems are starting to be interesting for the integration phase change materials. This study aims to show the state of the art of the main applications of phase change materials highlighting the latest trend and the research gaps that could open the door to future studies.

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TRENDS IN PCM DEVELOPMENT – FROM CALORSTOCK’94 TO ENERSTOCK’21

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Our planet is experiencing a profound transformation and it is very important to be prepared and also - if nature allows – be in control of this change. This final 2020 pandemic is telling us that we must think globally, act together, work constantly to adapt to these changes. Giving up cannot be an option. 20th century has been the age of fossil fuels that caused CO₂ in atmosphere to escalate very fast because of our greed for energy. Today CO₂ concentration exceeded alarming levels and has reached 415 ppm. The ultimate result is climate change – the clear and present danger – with implications far beyond the effects of pandemic and threatening future of world. In the “new normal” life after the 2020 pandemic, man needs to move on to the uninterrupted supply of clean and affordable energy sources immediately. This means using only renewables and local sources with higher efficiency.

Energy storage is the key enabling technology to reach this goal. There exist many ways of storing energy for thermal and electric generation. Some have been tried for thousands of years. Post-pandemic - Latent heat storage in Phase Change Materials (PCM) stands out with their versatility. PCMs with melting/freezing points in the range between -100 °C to 1000 °C can be tailored to be used in all kinds of applications in buildings, industry, agriculture, transportation and more.

We now need to view PCMs from a new perspective in the “new normal”, which above all needs uninterrupted digitization and promptness to severe changes. This necessitates having a closer look at the PCM development in the recent years. International thermal energy storage conferences, so-called “STOCK” conferences have been the most important venues where recent PCM studies were discussed. This paper aims to review the PCM papers presented at the last 10 “STOCK” Conferences [1-10] since CalorSTOCK’94 and reveal trends towards the new normal.

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ENERSTOCK 2021

Keynote lectures

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PHOTOCATALYTIC CO₂ AND CH₄ CONVERSION TO H₂ AND CO BEYOND THERMODYNAMIC EQUILIBRIUM FOR A POSSIBLE POWER TO GAS APPLICATION

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INTRODUCTION: Intermittent electricity production from wind farms is not synchronized with electricity consumption, thus generating substantial electricity surplus peaks. These peaks can be utilized for power to gas conversion, namely catalytic CO₂ reduction by CH₄ to H₂ and CO, in a highly endothermic reaction ($\Delta H=247$ kJ/mol). The main reaction product CO is valued in petrochemical industry, H₂ can be directed into the existing natural gas grids. Sunlight is a discontinuous, but endless energy source and technologies are sought to use it efficiently, thus minimizing societal dependency on fossil fuels. This contribution investigates photocatalytically accelerated CH₄ and CO₂ activation at low temperatures (≤ 500 °C) over Ni/CeO₂ catalyst using a combination of thermal (electric) energy and visible light.

MATERIALS AND METHODS: The CeO₂ was synthesized according to Zabilskiy et al.[10.1021/acscatal.5b01044] and 2 wt. % Ni was deposited as described by Zhang et al.[<https://dx.doi.org/10.1021/acscatal.9b04451>] The following characterizations techniques were employed: in-situ UV-Vis DRS, XRD, N₂ sorption, H₂-TPR, and TEM. Photocatalytic tests were performed between 190 and 500 °C using 2 mg of catalyst and equimolar CH₄-CO₂ flow (WHSV=600 L/gcat*h). The catalyst was illuminated by visible light (400 nm λ \leq 750 nm, 790 mW/cm²), concentrated to a spot with a 4.5 mm diameter.

RESULTS: TEM analysis revealed the CeO₂ support was rod shaped with approximate length of 100±20 nm and thickness of 20±5 nm. The average nickel crystallite size was 6±2 nm. The in-situ UV-Vis DRS recorded in 5% H₂/N₂ atmosphere at 450 °C revealed the absorption edge of CeO₂ and Ni/CeO₂ at 412 and 440 nm, which corresponds to bandgaps of E= 3.0 and E= 2.8 eV, respectively.

Self-sustaining thermocatalytic activity was observed above 355 °C over the Ni/CeO₂, giving a low H₂/CO ratio of 0.13. During the combined photo-thermocatalytic experiment over the same catalyst, H₂ and CO rates reached 4.7 and 8.5 mmol/gcat*min at 460 °C, respectively, which is ~2 times higher compared to the thermocatalytic run at identical catalyst temperature. The difference became even more obvious at lower temperatures: 10-fold higher catalytic activity at catalyst temperature of 355 °C. No methane and CO₂ conversion was observed below 350 °C in the thermocatalytic regime, whereas the photo-thermocatalytic reaction occurred down to 190°C. In purely photocatalytic mode at 190 °C, H₂ and CO formation rates of 0.058 and 0.36 mmol/gcat*min were recorded. Catalyst illumination with visible light increased the H₂ selectivity (reported as H₂/CO ratio) in the entire range of reaction temperatures. Arrhenius plots were used to quantify the effect of illumination on apparent activation energy (E_a) for CH₄ and CO₂, which equaled 125 and 120 kJ/mol in the thermocatalytic mode. The E_as were lowered to 30±3 kJ/mol for both CH₄ and CO₂ during the combined photo-thermo catalytic reaction. A change in reaction mechanism during photo catalysis and a substantial decrease in the activation barrier(s) of the rate determining step(s) of the DRM reaction is evident.

CONCLUSION: This work confirms the efficiency of visible light for accelerating the low-temperature conversion of CH₄ and CO₂ to syngas with simultaneously improving H₂ selectivity over Ni/CeO₂ catalyst.

ENERSTOCK 2021

WEDNESDAY, 9 JUNE 2021

ORAL PRESENTATIONS

DEVELOPMENT AND IMPLEMENTATION OF PTES IN COPENHAGEN

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INTRODUCTION: Large scale Pit Heat Thermal Storages (PTES) in Denmark have until now been implemented as long term storages combined with solar thermal plants. This kind of storages has been in operation since 2012 and monitoring programs have shown successful results for the best functioning plants. Danish district heating utilities in cities with large amounts of excess heat from waste incineration and/or industries in the summer period and also Danish utilities with large CHP plants have in a period made feasibility calculations for PTES in their systems. PTES are in many cases feasible, but the temperature level in a storage that is heated up to 90 oC as will be preferable if it is used as buffer tank for CHP systems is a challenge for the plastic liners used in the PTES combined with solar thermal systems. Høje Taastrup District Heating (distribution company) and VEKS (transmission company) in Copenhagen decided to meet this challenge three years ago and have been through a design and implementation process to be able to have a 70,000 m³ hot water storage in operation autumn 2021. This will enable the coupling of the heating and electricity sectors for increased flexibility of the overall energy system in Copenhagen. The storage will serve all CHP and waste incineration systems in Copenhagen.

MATERIALS AND METHODS: The main challenge in the development has been to find a polymer solution for tightening the storage. Polymer is used because it is cheap and can be welded. Solutions have been developed in cooperation with the HDPE supplier SOLMAX and in the Austrian research project giga_TES, where the material has been PP. Laboratory tests showed that PP can solve the temperature challenge. PP has a higher moisture diffusion than HDPE and that had to be taken into account when designing the lid construction. Also oxygen diffusion through the liner into the water resulting in risk of metal corrosion had to be taken into account.

RESULTS: The paper presents results on and discusses the following aspects:

- How the storage is integrated in the transmission and distribution systems in Copenhagen
- How the total DH and electricity production system is optimized during operation
- Development of liner solution
- Development of lid solution
- Cost analysis and analyzes of income
- Implementation experiences so far

CONCLUSIONS: PTES seem to be a feasible solution when flexible sector coupling and higher RES during transition to zero carbon district heating systems.

SIMULATION AND PERFORMANCE EVALUATION OF LARGE-SCALE THERMAL ENERGY STORAGE IN RENEWABLES-BASED DISTRICT HEATING SYSTEM

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INTRODUCTION: The integration of large-scale water-based seasonal TES (Thermal Energy Storage) into DH (District Heating) grids has gained increasing attention in the last decade. In the context of intermittently available renewable heat sources, TES systems are particularly favorable, being able to eliminate the time mismatch between energy supply and demand, representing therefore a key component of the new generation DH grids (Lund, et al. 2018). Such technology can indeed be coupled with several energy sources; solar thermal, Combined Heat and Power (CHP), industrial waste as well as geothermal can all benefit from the combination with TES, especially in the upcoming smart and flexible DH systems.

Considering the investment cost of a large-scale TES system, a preliminary study is necessary to guarantee the economic feasibility of the project, taking into account the availability of heat sources, the load requirements of the DH grid and the thermal capacity required from the TES (Ochs, et al. 2020).

MATERIALS AND METHODS: In a typical DH system, the heat supply side is represented by a combination of heat sources with different temperatures and time availability, while the load profile generally follows the ambient temperature, presenting a higher peak in winter and a lower peak in summer. The implementation of a 1-D equation-based TES model, coupled with a finite element method-based model of the surrounding ground provides a robust and reliable tool that can be used in the study of the behavior of large-scale TES systems (Tosatto, et al. 2019). Thus, COMSOL Multiphysics is used as main simulation tool, allowing the analysis and comparison of different TES construction types. Generally, different shapes can be adopted for TES systems but in this paper three main geometries are analyzed: buried tank, pit and shallow pit. The selection of a more appropriate shape is based on different criteria, which take into account the costs (e.g. land, excavation, materials, maintenance) and the energy and exergy performance. The geometry of the system has indeed a major impact on the distribution and amount of thermal losses, being them related to the internal thermal stratification of TES and to the external ambient conditions. Another important aspect, which must be taken into account in the design phase, is the influence of the TES on the surrounding soil: many legislations impose a limit on the soil temperature. Thermal insulation is therefore a crucial aspect to satisfy this requirement: its influence on both thermal losses and soil temperature is evaluated in the paper. Then, the use of Key Performance Indicators (KPIs) is used to compare the different TES options. In this analysis, two efficiency measures are introduced, defining the storage-efficiency (as the ratio between the energy actually recovered from the TES and the energy input) and the discharge-efficiency (as the ratio between the energy actually available and the maximum storage capacity). As pointed out by Dahash et al. (Dahash, et al. 2020), the geometry of the system plays an important role on vertical thermal stratification. The Stratification number ($Str(t)$) is therefore introduced to evaluate the ability of the analyzed systems to maintain a good stratification during the operation cycle.

RESULTS: The three geometries are analysed under the same boundary conditions (ambient temperature, ground properties). The same curves for the DH load demand and heat source availability are adopted to evaluate which one of the studied systems could provide the best coverage of the winter peak demand. In this perspective, the insulated buried tank TES appears to outperform the pit and shallow pit. The main reason behind this is that TES cover is the most critical part of the envelope, being in contact with the

ENERSTOCK 2021

Oral lectures

external environment and with the high temperature top water layers. The smaller cover surface of the tank results therefore in lower thermal losses, thus keeping a better thermal stratification.

CONCLUSION: Modeling and simulation are key steps in the preliminary design of large-scale TES: the selection of the proper shape, insulation characteristics and volume can be defined according to the available heat source and of the DH load requirements. This guarantees a proper allocation of the cost and an efficient operation of the overall system.

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EXPERIMENTAL INVESTIGATION ON A NEW HIGHLY EFFICIENT REGENERATION PROCESS FOR THERMOCHEMICAL ENERGY STORAGE

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INTRODUCTION: Thermochemical energy storage is a key technology to realize highly efficient thermal energy storages for various applications such as solar thermal systems or cogeneration systems. By storing the heat in form of chemical or physical bonds of special materials the energy can be stored almost loss-free over extensive time periods. At the same time a high energy storage density can be achieved. Both criteria are crucial, especially for compact long-term thermal energy storage applications. In order to obtain a high energy storage density, comparatively high temperatures of in excess of 180 °C are typically needed during the regeneration process. This is a drawback especially for solar thermal systems.

MATERIALS AND METHODS: This paper presents first experiences with the new and improved process for solar thermal charging of a zeolite sorption storage system. With the developed process, the required desorption temperature has been significantly reduced, which leads to a significant increase in the efficiency of the solar thermal system.

Within the national research project SolSpaces a new solar heating system has been developed, aiming to supply the demand for space heating of energy efficient buildings completely on a solar basis. The core element of the system is a sorption store, serving as seasonal energy store. The solar heating system has been installed in a compact research building for the purpose of testing and demonstration. The building (living space approx. 45 m²) has an annual heating requirement of approx. 2600 kWh/a. The storage system has a volume of approx. 4 m³ and a storage capacity of approx. 700 kWh. A 25 m² of vacuum tube air collector provides the heat for charging the store. The heating system has been under monitoring for several years. With a solar fraction of approx. 80% the results achieved are very satisfactory and correspond to the predicted performance.

The high storage capacity of approx. 150 kWh/m³ (factor of 2.5 compared to a hot water store at ΔT 50 K) is achieved by using a storage material of binder-free zeolite 13X. This zeolite is characterized by a very high water absorption capacity, it has excellent kinetics and a high adsorption enthalpy. These are very favorable properties for compact energy storage. On the other hand, Zeolite 13 X requires high desorption temperatures. Temperatures of 160 to 200 °C are necessary to achieve the desired high energy storage capacity. By using highly efficient solar collectors it was possible to reach desorption temperatures of up to 180 °C in this project. However, it is clear that the lower the desorption temperature, the higher the efficiency of the solar system. The combination of sorption storage system and solar collector we are therefore dealing with opposite efficiency behavior.

RESULTS: How can we succeed in lowering the required desorption temperatures and still achieve a high storage capacity? We have first dealt with this question in 2013. Based on theoretical considerations, we have presented a process that leads to a higher overall performance of the system despite a significantly reduced desorption temperature [1].

In this new desorption process, the desorption temperature is lowered by pre-drying the ambient air drawn in for the desorption process. With very dry air, zeolite can be regenerated to a large extent already at significantly lower temperatures. For example, the starting situation is zeolite with a water load of 295 g H₂O per kg of zeolite. For desorption, ambient air with a water vapor pressure of 15 mbar is used (corresponds to about 21 °C, 60 % relative humidity). A desorption temperature of 180 °C results in a residual load of 90 g/kg (residual load: amount of water that is still bound in the zeolite after desorption). If

the desorption is carried out with ambient air of the same humidity at 130 °C, the residual load increases to 154 g/kg. To dry the zeolite at 130 °C, the water vapor content of the air used for desorption must therefore be reduced. In the selected example, the air is pre-dried to a water vapor partial pressure of 0.5 mbar, resulting in a residual load of 72 g/kg after desorption. This means that by pre-drying the air, not only the desorption temperature can be lowered, but even an increase in storage density is possible. In this example, an increase of the storage density by 11 % is achieved.

Now, about seven years later, we have succeeded in implementing this process on a real scale in a real plant and testing it under real operating conditions. The technical effort for integrating the air-drying process into the heating system is comparatively low.

CONCLUSION: The functionality of the new desorption process has been demonstrated for the first time in a solarthermal heating system under real operating conditions. An energy analysis, which was carried out showed the strengths of the newly developed process. These are:

- Significant increase of the system efficiency:
 - More efficient operation of solar collectors
 - Longer operating times of the solar collectors and thus higher solar yields, since the lower regeneration temperature is reached faster
- Reduction of heat losses in the collector circuit and in the sorptive heat storage system
- Increase of the effectively usable storage density of the storage material

The first results of the new regeneration process show an enormous potential for the further development of sorptive heat storage systems. Thanks to the low-temperature regeneration process, zeolites can now also be used in applications in which other storage materials with lower desorption temperatures (such as silica gel or salts) were previously used. This is of great advantage for the process design, as zeolites are characterized by very good adsorption properties (compared to silica gel or salts) and high storage densities.

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EXPERIMENTAL RESULTS OF A 182 KWH THERMOCHEMICAL HEAT STORAGE SYSTEM FOR DOMESTIC APPLICATIONS INTEGRATED IN AN ORPHANAGE IN WARSAW

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A closed seasonal thermochemical storage system on salt hydrate basis was developed in the context of the Horizon 2020 project CREATE. The developed thermochemical storage system is designed to store heat seasonally for domestic applications in multi and single-family houses. The manufactured modules function as a fixed bed reactor and feature a modular prismatic design that is optimised towards compactness and each have a finned heat exchanger, exchanging heat between the storage material and the heat distribution system. The storage material used is granulated potassium carbonate; the modules were each filled with 400L of potassium carbonate forming a full-scale thermochemical storage system with a storage capacity of approximately 182 kWh. Additionally, a simple and inexpensive evaporator/condenser was designed and implemented as part of the storage system.

The thermochemical storage system was tested in a laboratory in Gleisdorf, Austria. Hardware in the loop experiments, similar to the future use case (incl. buffer storage tank, heat pump, low-temperature source and, solar system) were performed, where detailed measurements were recorded for over 300 parameters. After the completion of these experiments in July 2019, the thermochemical storage system was transported to Warsaw and integrated into a demo house, an orphanage where 2 adults and 8 children live, for a practical demonstration. The storage system was integrated in the existing domestic hot water and space heating system.

Experimental results of the hardware in the loop experiments which for example will be presented in detail are the measured power output, depending on the module inlet temperature (up to 1.93kW at 30C), as well as the packing and storage density (115kWh/m³ on module level) and cycling stability of the system. Furthermore experimental results of the real scale demonstration (operating behavior, loading via solar and unloading into the heating system) in the orphanage in Warsaw will be presented.

COATED $\text{Ca}(\text{OH})_2$ GRANULES FOR THERMOCHEMICAL HEAT STORAGE: REAL-TIME VISUALISATION AND ANALYSIS

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INTRODUCTION: The gas-solid reaction $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Ca}(\text{OH})_2(\text{s}) + \Delta\text{H}$ is promising for the application of heat storage for power generation or as waste heat recovery in industrial processes. For this reason, different reactor concepts have been investigated for this thermochemical storage system. Among them, the moving bed concept is of particular interest as it allows to decouple power and capacity. Nevertheless, some properties of the powder $\text{Ca}(\text{OH})_2$ hinders the movement of the material under reaction conditions and the bulk clogs in the reactor. To address this issue, different modifications on the powder $\text{Ca}(\text{OH})_2$ have been developed. One approach is the coating of pre-granulated $\text{Ca}(\text{OH})_2$ with Al_2O_3 nanostructured particles. The samples were successfully tested in a lab-scale moving bed reactor developed in DLR and showed good results in terms of cycling stability and energy density. However, the movement of the granules through the reactor was only partly achieved which requires a deeper understanding on the behaviour of a bulk of granules in the reactor tubes.

MATERIALS AND METHODS: In order to understand how the modified granules get stuck in the heat exchanger tubes, a special experimental device was developed. The setup emulates the conditions present in the reactor tube at water vapour pressures from 0-2 bar and temperatures of 350-540 °C and enables the visualisation of the reacting material in real time. A high-resolution camera equipped with a macro lens takes images of the reacting granules inside the device. With this set up, the influence of three different parameters, the diameter of the pre-granulated $\text{Ca}(\text{OH})_2$, the coating additive and the thermal pre-treatment, is analysed in a 5-fold cycle experiment series. With the images obtained the change in dimensions, degree of deterioration and formation of clusters between the granules during the hydration/dehydration experiments can be determined. By additional TGA and compression tests the cycle stability and crushing strength of the samples are determined.

RESULTS: The first results show that the area of the granules coated with Al_2O_3 increased by 17% during hydration and decreased by 10% during dehydration. Despite the changes in volume, the overall shape was maintained. Thus, the additive improves the stability of the granules over cycles.

CONCLUSION: This contribution will present the first real-time visualisation of reacting $\text{Ca}(\text{OH})_2$ granules during experiments. Overall, there is a positive effect of the Al_2O_3 additive on the structural integrity of $\text{Ca}(\text{OH})_2$ granules. The presentation will discuss the influence of different parameters of the granules on their stability and the results will reveal important insights for future design of heat exchangers for granulated materials.

EXAMINING ZEOLITIC IMIDAZOLATE FRAMEWORKS (ZIFs) FOR THERMOCHEMICAL HEAT STORAGE AND REALLOCATION

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INTRODUCTION: The increasing demand of heating/cooling is of grave concern due to the ever increasing population. Since energy for heating and cooling represents up to 50% of world final energy consumption, there has been an increased interest in finding environmentally friendly methods for the optimization of heat supply/demand. One method that addresses this issue and uses renewable energy is Thermal Energy Storage (TES), which uses the reversible chemical reactions and/or sorption processes of gases in solids or liquids. One major benefit of using this method is that it only shows an insignificant amount of heat loss while reaching a considerably higher energy storage density. Sorption thermal energy can be examined using traditional adsorbents (e.g. zeolites) or innovative adsorbents (e.g. metal-organic frameworks). One of the subgroups of MOFs is Zeolitic imidazolate frameworks (ZIFs), which are comprised of transition metal ions (Zn, Co, etc.) and imidazolate linkers. ZIFs are structured similarly to zeolites with where the metal ion replacing the Si/Al and the imidazolate linker replacing the O atoms. We examined ethanol as an adsorbate, since it has seldom been explored for this purpose but may prove to be beneficial for applications at lower temperatures when compared to water.

MATERIALS & METHODS: The ZIFs studied were selected based on their reported pore sizes and pore capacities. [1] ZIF-8 and ZIF-90 were selected due to both have large pore entrances and pore volumes. For comparison purposes ZIF-74, which has a significantly lower reported porosity was studied. [1] ZIF-8 and ZIF-90 were synthesised using optimised methods based on literature. ZIF-74 was synthesised by significantly modifying the method published by Banerjee et al. (2008). [2] The samples used zinc nitrate (ZIF-8 and ZIF-74) or zinc acetate dehydrate (ZIF-90) as the zinc precursor. The linkers used were 2-methylimidazole (ZIF-8), Nitroimidazole (ZIF-74), 5,6-dimethylbenzimidazole (ZIF-74) and 2-Hydroxyisocaproic acid (ZIF-74). TG showed that ZIF-74 did not require activate. The activation of the two other ZIFs was achieved via drying in a vacuum over at 150°C (ZIF-8) and soaking in methanol for 6-8 hours followed by drying in vacuum oven at 150°C overnight (ZIF-90). All ZIFs were characterised using XRD, TG and BET. Ethanol sorption analyses were performed by an IGA-100 gravimetric analyser (Hiden Isochema Ltd.). The isotherms were collected at two different temperatures (25°C and 30°C or 25°C and 35°C) in the relative pressure range from 0 – 0.9.

RESULTS: Structural properties were examined using XRD, TG, and nitrogen physisorption which revealed phase pure products. The crystalline structures of the three ZIFs were confirmed using XRD and comparing to the simulated diffractogram pattern. This analysis was repeated after the activation method to ensure that crystalline structure had remained intact. TG analysis was completed prior and after the activation of ZIF structures to ensure that any solvents present were removed during activation but the remaining structure hadn't collapsed. BET analysis showed that the ZIFs had a specific surface area of up to 1118 m²/g. The IGA results showed that the capacity up to 35 wt. % ethanol could be reached and that mechanism of sorption of ethanol in selected ZIFs were dominated by diffusion limitations of the molecules through the pores. The structures remained crystallinity after the tests. Sorption capacities and related adsorption enthalpies will be further discussed in the contribution. Based on the all the results for the three ZIFs, the pore capacity and pore size has a direct impact on the surface area and the % ethanol uptake. ZIF-8 and ZIF-90 which have the larger pore size and pore capacity show significantly better results in comparison to ZIF-74.

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CONCLUSION: The evaluation of three ZIFs as sorbents for sorption based energy storage by using ethanol as sorbate revealed a stable system suitable for potential use in TES.

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SWS COMPOSITES BASED ON LiCl FOR SORPTION THERMAL ENERGY STORAGE: THERMOCHEMICAL AND KINETIC PROPERTIES

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INTRODUCTION: The present work concerns the development of a composite sorbent material, which will be employed for the validation of the operation of a sorption thermal energy storage system in various cold climatic zones in Europe. The composite material, defined also selective water sorbent (SWS) family, is specifically synthesized based on commercial mesoporous silica gel (as host matrix) and LiCl (as filler). This paper focuses on the performed activity for the preparation and characterization of the sorbent, evaluating its thermochemical and kinetic properties. Finally, preliminary calculations of the achievable thermal energy storage density were performed to compare the results with other materials reported in the literature.

MATERIALS AND METHODS: Based on a preliminary screening of commercial materials and expected thermodynamic performance, for the synthesis of the SWS the selected porous matrix was a mesoporous silica gel, namely silica gel by Sorption Technologies (SGST). Lithium chloride with technical grade purity (> 95%) was used as a filling salt. Two samples were prepared at different salt concentrations; namely, 30 wt.% and 35 wt.% to investigate the effect of the salt content on both thermal energy storage density and dynamics.

The equilibrium isobars of the SWS were measured by a DVS vacuum analyser at various vapour pressures to verify the SWS sorption capacity and to evaluate the achievable storage density.

A modified TG/DSC apparatus (i.e. Setaram LabsysEvo) was employed in order to directly measure both sorption capacity and enthalpy of sorption at the evaporation temperatures of 5°C and 10°C. Kinetic characterization of the optimized samples were performed by means of a Volumetric Large Temperature Jump apparatus, able to mimic the real operating conditions of the seasonal storage.

RESULTS: The equilibrium isobars were evaluated both during adsorption and desorption under the defined evaporation and condensation pressures. In particular, the adsorption branch was considered for $T_{ev}=5$ °C/ $P_{ev}= 9.0$ mbar, while the desorption branch was considered for $T_{con}=30$ °C/ $P_{con}=42.9$ mbar and $T_{con}=35$ °C/ $P_{con}= 56.7$ mbar. In such a way, possible hysteresis effects between adsorption and desorption phases are properly considered. From the evaluation of the ad/desorption isobars, it is evident that the larger the amount of confined salt, the higher sorption capacity of the composite. No relevant hysteresis were observed with the measurements.

DSC/TG curves highlight that the highest performance can be reached with an evaporation temperature of 10°C and with the sample 35% LiCl/SGST. This represents the case in which low temperature solar thermal heat is available during wintertime to support the evaporation process.

It turned out, that the kinetic performance is not strongly affected by the hydration/dehydration reaction between the salt and the water vapour. The sample with the high salt concentration showed a higher differential water uptake and a higher adsorption dynamics than the low salt concentration sample, revealing higher energy storage and power densities.

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CONCLUSION: The obtained results confirmed the possibility of achieving up to 1.0 GJ/m^3 of energy storage density under real operating conditions at material level, with a projected discharging power suitable for typical space heating demand profiles.

INVESTIGATIONS ON THE WATER-ADSORPTION CHARACTERISTICS OF A NOVEL COMPOSITE MATERIAL THAT COUPLES ADSORPTION AND SENSIBLE HEAT STORAGE PARTICLES

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INTRODUCTION: Wet cooling towers are no longer viable solutions in water-scarce regions because they consume up to 4m³/kWh (90 to 95% of the water consumed by a power plant) [1]. The use of dry coolers reduces up to 80% of water consumption [2], however, the efficiency of the turbine decreases significantly if the temperature of ambient air exceeds 20°C [3]. This leads to additional investment and increase the final electricity cost. In the past decade, works on the use of cTES (for cold Thermal Energy Storage) systems [4] have shown the potential to enhance dry coolers performances by storing the power block heat during the day and evacuating it during the night, when ambient temperatures are colder. More recently, the French Carnot COOLSTO project improved this concept by adding thermochemical heat storage in an overall cTES system [5]. The system reactor was based on the use of atmospheric air as cold source and a double granulometry packed bed composed of polished glass beads and a Regular Density Silica Gel (RDSG) grains acting as a sensible heat storage and sorption materials respectively. COOLSTO project results clearly demonstrate the relevancy of this coupled approach [6].

The current objective is to improve this concept by using a coated version of an AQSOA Z05 zeolite on the previously mentioned glass substrate. In this study, we investigate the water adsorption-desorption characteristics of this novel composite material thanks to a coupled Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) under controlled humidity. The first aim is to measure the thermodynamic and kinetic behavior of the zeolite used for the fabrication of the composite material and to compare it against literature data [7, 8]. The second series of tests aim at checking that the zeolite embedded in the composite keeps the same behavior than the pure one.

MATERIALS AND METHODS: The novel material is mainly composed of polished glass beads with a diameter of 16±0.8 mm coated by fine powder of zeolite with a D90=5µm using the patented method [9]. The coating is composed by a mixture of the zeolite powder (5%wt) with a water-vapor permeable membrane (5%wt). Recent works on the thermodynamic behavior of the AQSOA Z05 and the RDSG [7, 8] show that both materials are related to working temperatures comprised between 20 and 100°C. The first one shows a type V isotherm (according to BET theory [10]) raising between 15% and 35% of relative humidity (RH) [7, 8], while the latter one shows a type I isotherm raising between 0% and 50% of RH [7].

Up to now, a complete study of water adsorption-desorption on AQSOA Z05, under static and dynamic conditions, is not available in literature. The isotherms presented in both [7, 8] have a similar form, but the proposed models diverge in the studied conditions and there is a lack of experimental data on desorption kinetics.

In this work, the water adsorption-desorption behavior of both the Z05 and the coating samples are measured by a TGA-DSC analyzer under a flowing nitrogen controlled atmosphere for the temperatures ranging from 20°C to 60°C and the RH up to 70%. The samples are placed in a quartz crucible inside the reaction chamber, which has a radiant heater for maintaining a constant temperature. The vapor charging flow rate is controlled automatically by an external vapor generator. During the experiments, the humidity and temperature of both the reaction chamber and the vapor generator are controlled within acceptable

error ranges ($\pm 0.8\%RH$ and $\pm 0.1^\circ C$). The samples mass variations are measured by a high accuracy ($\pm 0.01\%$ precision) hang down symmetrical beam balance based on a horizontal beam and an electro-optical equilibration system, which is maintained outside the reaction chamber.

The thermodynamic characterization consists in measurement of samples mass and heat variations compared to an inert reference at given conditions of temperature and RH. The aim is to maintain the samples at constant conditions until they reach the equilibrium state, measure the maximum values of water vapor uptakes and trace their isotherms. The kinetic data is also obtained while measuring the mass variations of the samples as a function of time. However, the thermodynamic determines the maximum uptakes at given temperature and RH, while the kinetic determines the amount of time taken for the reaction to reach these equilibrium states.

RESULTS AND CONCLUSIONS: The thermodynamic data obtained for the AQSOA Z05 shows it to be more suitable than the RDSG for a day-night thermal storage system, in which the conditions of the air may vary from $T=40\pm 5^\circ C$ and $HR=45\pm 15\%$ to $T=20\pm 5^\circ C$ and $HR=20\pm 5\%$. The adsorption isotherms presented in this work are suited to use in modelling of sorption processes such as those occurring in, for example, packed bed reactors. Next steps include tests of the kinetic behavior and new experimental campaigns with 250kg of the novel composite material. The experimental data base will allow validating a numerical model that is under development. The development and the validation of a coupled sensible-sorption model are of major importance to analyse what happens inside the storage reactor and to enhance operation and control. Such validated model is necessary to test different configurations depending on the locations and related weather, and to assess the techno-economic interest of the concept.

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WATER COMPOSITE SORBENTS BASED ON GAMMA ALUMINA FOR SOLAR SORPTION HEAT STORAGE

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INTRODUCTION: Thermochemical energy storage as one of the thermal energy storage (TES) technologies offers reduction of fossil fuels utilization, which is currently dominating the heating sector. Tremendous recent progress in the material science revealed some novel composite sorbents with confined hygroscopic salts in porous matrices, which show high heat storage capacities under different operating conditions. The main advantage of these sorbents is the possibility of tailoring their performance due to the wide availability of different porous structures from silicagel to vermiculite and hygroscopic salts (LiCl, CaCl₂, SrBr₂, MgSO₄,...). To effectively design the composite sorbent, it is necessary to first examine structural properties of the matrix and of the composite, which are determining its sorption properties and storage final efficiency. To optimize these properties new synthetic and post-synthetic approaches should be developed.

A study on the influence of the structural properties of the composites of the low cost commercial granulated gamma alumina and mesoporous gamma alumina prepared at National Institute of Chemistry with different salt hydrates on water sorption is presented. Furthermore, the effects of the salt type on matrices and on the water sorption capacity of the composites were investigated. The influence of synthesis paths of the mesoporous gamma alumina matrix on sorption capacity was studied. Water sorption properties of the composites were studied for low-temperature heat storage application.

MATERIALS AND METHODS: Mesoporous gamma alumina was synthesized by hydrothermal synthesis using different surfactants. The syntheses were performed at different calcination temperatures. The composites were prepared by incipient wetness impregnation and melt infiltration.

RESULTS: Altering the synthesis parameters had a significant impact on structural and sorption properties like specific surface area, pore width and water uptake. Namely, as the calcination temperature lowered and molecular weight of surfactants increased, the specific surface area and the water uptake increased. The results showed that water sorption capacity of composite materials depends on the structural properties of the matrix, the amount and type of hygroscopic salt and the preparation of the matrices and their` composites. Water sorption capacity of granulated alumina determined at 0.4 p/p₀ was 0.09 g/g, while its composite containing 20 wt. % of CaCl₂ showed water uptake up to 0.45 g/g. Lower water uptake (0.29 g/g) was determined for the composite with 20 wt. % of MgCl₂.

CONCLUSION: The composite of low cost granulated gamma alumina and 20 wt. % of CaCl₂ can achieve high energy storage capacity of 500 kWh/m³ under boundary conditions: desorption temperature at 100 °C, adsorption temperature at 30 °C and dew point temperature of 10 °C.

THE 4-TEMPERATURES-APPROACH – A METHOD TO EVALUATE THERMOCHEMICAL HEAT STORAGE MATERIALS UNDER APPLICATION CONDITIONS

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INTRODUCTION: Thermochemical heat storage offers the possibility to achieve high thermal energy storage capacities compared to sensible heat storage. To assess the actually achievable storage capacity of a thermochemical heat storage, an evaluation under conditions given by possible applications of such storage systems is necessary. The proposed approach in this work – the so-called 4-temperatures-approach – delivers an easy to define first step toward a realistic testing and evaluation of thermochemical reaction pairs for certain energy relevant applications. The four relevant temperatures are the available charging temperature applied to the storage, the temperature supplied to the consumer, and the ambient temperatures during charging and discharging. As an example, the approach is applied to testing the sorption pair zeolite/water under the conditions of the application of seasonal storage of solar thermal heat for domestic heating purposes.

MATERIALS AND METHODS: Experiments were performed with a test device that is dedicated to measure breakthrough curves of a packed bed of zeolite exposed to a humid air stream. In the experiments, the temperature lift, the water uptake (during adsorption), and the achieved storage capacity can be measured. The ambient dew point for desorption and the air temperature for adsorption (22 °C) were kept constant for all experiments. The desorption/charging temperature was 180 °C or 140 °C and the available humidity/dew point for adsorption/discharging was 8 °C or 17 °C. The fourth temperature, the temperature delivered to the consumer, is a measured result of the experiment.

RESULTS: The results show how sensitive the achievable storage capacity depends on the chosen temperature levels. The highest dew point during adsorption (17 °C) leads to the highest outlet air temperature of about 63 °C. This is caused by the highest amount of water adsorbed per air mass, releasing the highest amount of adsorption enthalpy per air mass. Lower dew points (8 °C) lead to lower outlet air temperatures of about 43 °C. In this case, the outlet temperatures drop after 6 or 7 hours, depending on the desorption temperature (140 °C or 180 °C). A higher desorption temperature keeps the outlet temperature at a high level for a longer time. Under the chosen application conditions, the measured storage capacity is between 50% and 67% of the maximum reaction enthalpy.

CONCLUSIONS: The introduced method of four temperatures describing the operation conditions given by an application leads to a more realistic evaluation of the achievable storage capacity of thermochemical energy storage. Experimental results for the sorption pair zeolite/water show that the achievable storage capacity can be substantially reduced in comparison to the maximum reaction enthalpy of the thermochemical process.

DEVELOPMENT AND CHARACTERIZATION OF A LiCl BASED SILICONE FOAM FOR THERMAL ENERGY STORAGE APPLICATIONS

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INTRODUCTION: The development of high performing and stable Thermal Energy Storage (TES) materials is considered as a relevant topic in order to further promote and improve the use of renewable energy technology and to enhance the energy efficiency. TES materials can be classified in three categories: sensible, latent and thermochemical ones. The latter category is considered a very attractive option due to the achievable high energy storage density and the possible applicability in long-time energy storage. Thermochemical TES storage is based on the interaction between sorbent and sorbate, characterized by a low binding energy, making possible to operate effectively even at low and medium temperatures (e.g. 80-150 ° C). Several investigations of thermochemical TES have been reported by using pure salt hydrates. These materials led to some applicative issues during charging/discharging cycles (such as agglomeration, corrosion and swelling) coupled to low heat transfer efficiency and not fully reversible sorption storage reaction. In order to overcome these issues, a recent approach was proposed, based on the embedding of salt hydrates in a macro-porous and permeable to water vapor structure.

MATERIALS AND METHOD: This strategy was effectively proposed to assess the performance of a composite material constituted by a polymeric macro-porous foam as matrix that host LiCl hydrated salt. The choice to encapsulate the salt within a permeable porous matrix could allow to inhibit the detrimental effects of aggregation or coalescence, thus limiting the related corrosion issues, without compromising hydration/dehydration capabilities. Furthermore, the flexible nature of the foam could add a beneficial effect on the mechanical and hydrothermal cycles stability during the hydration/dehydration process. Preliminarily a foam morphology and structure characterization were carried out in order to evaluate the composite material stability and homogeneity. Furthermore, a real-time in situ scanning electron microscopy (SEM) analysis was performed in controlled temperature and humidity conditions. This set-up was specifically proposed in order to assess the evolution of the material expansion and contraction during the hydration/dehydration stages of the salt.

RESULTS AND CONCLUSIONS: The results validated that the silicone matrix favor the interaction between the salt and the water vapor avoiding leakage phenomena in the composite material caused by salt deliquescence. This is a potentially effective result for simplifying handling, installation and maintenance steps of the TES system.

These results have been confirmed by hydration and dehydration tests by means thermo-gravimetric tests carried out on specimens subjected to increasing charge/discharge cycles; e.g. composite foam with 40 wt% LiCl reaches an adsorption capacity of about 200% indicating the effective hydration of almost all the filled salt. The results evidenced, also, an effective micro-thermal stability of the material, confirming its potential use for TES applications.

OPERATION AND CHARACTERISTICS OF A DIRECT CONTACT LATENT THERMAL ENERGY STORAGE

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INTRODUCTION: Related to the storage medium, latent thermal energy storage systems (LTES) can exhibit significantly higher energy densities than sensitive storage systems by utilizing the enthalpy of the phase change liquid-solid. In contrast, complex heat exchangers (HEX) which displace the storage medium in the tank reduce the energy density in relation to the tank volume and increase the storage costs. The HEX concept of direct contact comprises no physical HEX in the tank and thus promises to achieve high power and energy densities at low cost. The direct contact latent thermal energy storage (DC-LTES) has been scientifically investigated in sporadic studies since the middle of the last century. The studies mainly analyze thermodynamic research questions concerning heat transfer in the tank. Due to the design of the tank as a drop column reactor where the heat transfer fluid (HTF) flows directly through the PCM, the design and controlling of the setup are particularly complex and challenging. These challenges have been partially documented in previous literature but never analyzed in detail. This work focuses on the further investigation and analysis of the fundamental technical issues that occur in direct contact systems and proposes paths for their solution.

MATERIAL AND METHODS: In the present study the operation and operating characteristics of an optically transparent DC LTES setup with a volume of 55 l at different operating points are experimentally analyzed. As storage medium Tetrabutylammonium bromide-26 H₂O with a phase change temperature of 12°C and as HTF a synthetic thermal oil (Therminol® D12) is used. During the commissioning of the test-system, challenges had to be overcome that were not described in the literature before. To overcome these challenges, small-scale experiments are conducted and solutions are developed. After commissioning, test series are carried out which document the thermal behavior as well as the optical solidification and melting behavior.

RESULTS: A laboratory scale DC LTES system was developed which could be operated fully automated. The optical observations of the phase change processes are related to the thermal power curve. Thus, the factors dominating the process are identified and control strategies for increasing the efficiency are determined.

CONCLUSION: The maximum power and energy density of a DC-LTES system is characterized. The formation and stability of bulk dispersions between the HTF and the storage medium are recognized as the main limiting factor that needs to be overcome in order for the DC-LTES to be successfully commercialized.

INSULATION WITH CONTROLLABLE HEAT TRANSFER FOR THERMAL ENERGY STORAGE

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INTRODUCTION: The storage of thermal energy is fundamentally linked to the presence of mass. Conversely, the question comes up, if existing masses could be seen as potential thermal energy storages that can be thermally activated, e.g. by electric heating. In this way, building structures or even batteries in electric vehicles could be used as active thermal components.

Besides technical limitations, e.g. maximum temperatures, the prerequisite for thermally activating masses is the possibility to control the heat flux across the storage boundaries. In order to control this heat transfer, an adjustable insulation layer can be realized by using reversible gas-solid reactions in combination with porous insulation structures. The controllable insulation system accordingly consists of two coupled core components: a porous insulation material and a metal hydride reactor.

METHODS: Porous structures show a dependency of the thermal conductivity on their internal gas pressure, known as Knudsen effect. In the presented system, this pressure level in the insulation panel is set by a connected reversible endo-/exothermal metal hydride reaction system. By adjusting the temperature of the reacting metal hydride the pressure in the system can be controlled according to its equilibrium line. Since both components are coupled, a change in pressure is directly linked to a change in thermal conductivity of the porous structure according to its sigmoidal curve. As a result, the actual heat flux from any isolated system could be influenced by changing the temperature of a single, separate component.

RESULTS: At the German Aerospace Center in Stuttgart, a test bench was set up that allows for a separate investigation of the individual components as well as of the overall coupled system. The central challenge is the interaction of the key components, the insulating panel and the metal hydride reactor, in terms of matching pore sizes, pressure ratios and metal hydride materials. Therefore, in current work insulating materials with different pore sizes are tested in combination with different metal hydrides to better understand their interaction, to identify potential limitations and to approach optimal combinations that could be used for different applications. The experimentally gained proof of operability of the system will be presented as well as measurement results of different pore-sized vacuum panels and gas pressure ranges in terms of optimized switching factors of heat transfer rates.

CONCLUSIONS: Our recent experimental results show the general applicability of this kind of controllable heat transfer in the context of thermal energy storage. Consequently, our contribution will address critical properties of the individual components, show experimental results and discuss examples of potential applications.

LARGE HEAT PUMPS WITH HOT WATER STORE IN LOCAL HEATING SYSTEMS - INVESTIGATION OF OPERATION STRATEGIES

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INTRODUCTION: In the context of the German energy transition, heat pump technology utilizing heat and electricity from renewable sources is an alternative to traditional fossil fuel based boilers, which enables a sustainable heat supply. Within the project “Zwickauer Energiewende Demonstrieren (ZED)” (Demonstration of German Energy Transition in Zwickau), the transformation of an exemplary residential area in Zwickau city (Germany) into a zero-emissions district employing a heat-pump-based local heating system with hot water store is to be investigated. This project started as part of the funding initiative of the German Federal Ministry of Education and Research and the German Federal Ministry for Economic Affairs and Energy entitled “Solar Construction/Energy-Efficient City” and was launched in November 2017.

PROBLEM AND METHOD: In the present project, the heat pumps are supposed to use the return flow of an existing district heating network as heat source. Most commercially available heat pumps have a standard temperature spread from 3 to 5 K in the evaporator. In this case, the limited source flow rate in the project leads to a relatively low heat capacity of the heat pumps (output), which requires an unusual large dimension of the hot water store and impairs the economic efficiency of the heating system. To ensure an optimal store dimension, a possible solution is to install a mixing circuit on the heat source side of the heat pump to increase the temperature spread of the heat source by remixing the return water, whereby the coefficient of performance for heating becomes smaller. Another solution is to increase the temperature spread in the evaporator directly; also in this case, the coefficient of performance for heating diminishes. Here, we present the theoretical investigation of two heat pump configurations as well as operating modes: variant a) Installation of a mixing system in the heat pumps with standard temperature spread in the evaporator (5 K) and variant b) constant water flow through the evaporator with varying temperature spread up to 15 K. The heat pumps were simulated using the program EBSILON®Professional. The heat source flow rate is limited to 78.5 m³/h in winter and 52.33 m³/h in summer. The water inlet temperature of the evaporator is assumed to be constant at 50 °C. With the operating data of a compact speed-controlled screw compressor obtained with the design software from BITZER, after calculating the theoretical refrigeration cycle with an isentropic compression in the software REFPROP, the isentropic efficiency of the compressor under part-load conditions can be determined and implemented in the heat pump model. Two performance indicators are applied to evaluate the energy efficiency of the heat pump variants: coefficient of performance for heating (with consideration of the power consumption of the feed pumps on the heat source side) and annual coefficient of performance for heating, which is obtained by dividing the annual produced heat energy by the annual energy consumption of the compressor and the feed pumps on the heat source side.

RESULTS: The heat pump variant b) has a significant larger capacity range (up to approx. 1750 kW) than the variant a) (up to approx. 900 kW). Also, the coefficient of performance for heating of the variant b) is higher than that of the variant a) from approx. 750 kW. The system simulations with consideration of the hot water store operation show that the heat pumps in variant b) achieve a better annual coefficient of performance for heating (approx. 4.6) than in variant a) (approx. 3.3). In the presented case, the energy consumption of the feed pumps on the heat source side has less influence on the energy efficiency performance. Besides, the insufficient heating capacity of the heat pumps in variant a) results in heat undersupply in winter and

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Oral lectures

hinders the efficient utilization of the hot water store, which achieves 30 % less storage cycles with variant a) than with variant b).

CONCLUSION: Heat-pump-based ecological district heating system has promising potential for the transformation of many existing residential areas into zero-emissions districts. The hot water store decouples heat pump operation from heat load to ensure that the heat pumps always work at the optimum operating points. Optimization of heat pump configurations and operating modes according to the local boundary conditions can improve the annual coefficient of performance for heating as well as the efficient utilization of the thermal energy store.

VERTICAL ROCK BED FOR HIGH TEMPERATURE ENERGY STORAGE: PILOT PLANT FINDINGS

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INTRODUCTION: An increasing amount of countries strive for ambitious greenhouse gas reductions within several frameworks on national and global level. But already today, the increasing penetration of renewable energy sources causes challenges in the power sector due to the fluctuating nature of wind and solar power. Therefore, more flexibility is required on the power generation and consumption side as well as for power transmission and distribution. One promising flexibility option are large scale energy storages. Rock bed storages are suitable for grid-scale applications due to low-cost as well as high temperature resistant and environmental harmless materials. Furthermore, sector coupling and power plant retrofits are conceivable. As part of Energy Technology Development and Demonstration Program (EUDP) from the Danish Energy Agency, DTU Energy built two rock beds for storing heat at temperatures up to 675 °C. This presentation will share the design concept as well as experimental results for the 3,2 m³/ 1 MWh thermal energy storage with vertical flow orientation including a post-operation inspection.

MATERIALS AND METHODS: The unpressurized gas/solid packed-bed storage uses atmospheric air as heat transfer fluid and volcanic rocks in two different sizes as storage material. It consists of a hemispherical housing (entrenched in the ground) which is covered by a conical top and therefore avoids thermal ratcheting. Air enters and exits the rock bed in vertical direction to use natural stratification to its advantage. Additionally, the flow direction for charge and discharge is reversed to obtain a flat thermocline. Together with the three heaters, inlet and outlet pipes can be located on top of the storage by employing a flow manifold inside the storage. Effects of operational conditions are studied in >100 experiments and post-operation inspection includes a storage disassembling as well as thermal degradation studies in the lab.

RESULTS: The maximum output power can be supplied within less than 5 minutes. The increase of heater set temperature from 600 to 675 °C lead to slightly lower charge efficiencies but higher output power as well as temperature stability. Compared to the previous horizontal flow storage¹, round trip efficiency increased from 68,43% to over 90%. Consecutive cycles (each with 24h charge, 24h rest, 24h discharge) proved mechanical soundness. Even though a slight destratification is observable during each rest, higher charge efficiencies occur for higher number of cycles due to heat stored in the external thermal mass. The post-operation inspection showed rock rearrangement due to thermal ratcheting in the cone part leading to gaps between cone wall and rock bed. However, >3000h high temperature cycling did not significantly affect the rock stability even though the effect of heat exposure is observable on macro- and microscopical level.

CONCLUSION: Novel design concept solved issues regarding rock bed temperature distribution as well as mechanical implementation. Individual as well as consecutive cycles showed upscaling readiness and improved performance compared to previous storage¹. Due to post-operation inspection, further design improvements and rock stability confirmation are worked out.

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THE IEA ENERGY STORAGE TCP TASK 36 – A WORKING GROUP ON CARNOT BATTERIES

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Carnot Batteries are an emerging technology for the inexpensive and site-independent storage of electric energy. Also referred to as “Pumped Thermal Electricity Storage” (PTES) or “Pumped Heat Storage” (PHES), a Carnot Battery transforms electricity into thermal energy, stores the thermal energy in inexpensive storage media such as water or molten salt and transforms the thermal energy back to electricity when required. Carnot Batteries have the potential to solve the global storage problem of renewable electricity in an economic and environmentally friendly way.

Task 36 of the IEA energy storage Technology Collaboration Programme aims to establish an international platform that brings together experts from industry and academia. It offers a place for the community to systematically investigate and discuss different Carnot Batteries technologies and their potential role in a future energy system.

The key objective of Task 36 is to collect and provide information for all stakeholders. Therefore, its workplan includes the mapping of the main Carnot Batteries technologies, the development of key performance indicators and a critical assessment of the technological competitiveness and R&D demand. The working group tries to help the technology to market and delimit its market reach by identifying the services that should be or can be provided by Carnot Batteries, by informing policy makers and by providing a basis for proper regulations. International dissemination of the technologies through workshops, white papers, open source datasets and scientific papers is also part of the workplan.

The present communication will provide an overview of Task 36 along with its current status and its participants. The communication will outline the results that have already been achieved as well as the upcoming work program for Task 36.

COMBINED HEAT AND POWER COAL FIRED PLANTS – THE BEST CHOICE OF EARLY GRID-SCALE CARNOT BATTERIES APPLICATIONS

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INTRODUCTION: In Czechia alone, 1.6 million households, 40% of the population, relies on central and district heating systems. Nearly all the heat is produced from fossil fuels, mostly coal fired combined heat and power plants (CHPP). Even though the cogeneration provides high efficiency of fuel utilization, there is a large effort for phasing out of the coal. As these CHPP are industrial sites with high capacity electrical grid connection, thermal grid connection and used for flexible operation and typically having a lot of auxiliary space (mostly from being previously oversized), they are the ideal site for Carnot batteries, which already provide electricity and heat in the time of high demand.

MATERIALS AND METHODS: Adding thermal storage at parameters sufficient for steam production for the existing turbine is only a minor investment in comparison to building a whole new power plant. The steam cycle with the extraction turbine is already optimized for a flexible ratio between power and heat production. Locations around major cities provide geographical benefit of sitting these Carnot Batteries near major power consumers and being distributed across the country for a resilient system allowing effective utilization of electrical price volatility and allowing integration of additional renewables into the grid.

RESULTS: In the presentation, after introducing the concept and its benefits, we present a case study based on a specific coal fired CHP plant in a small town in Czechia. The proposed system is described. It is based on direct electrical heating on the power to heat process, thermal energy storage based on either molten salts or gravel packed bed and finally heat exchangers are integrated to work as steam generator integration. Sizing of major components in comparison with existing technologies is shown. The regimes of operation and expected revenue streams of the proposed system are presented on a case study.

CONCLUSION: In the conclusion as shown, that the CHP plants are suitable for conversion into the Carnot battery systems as they can work in the power to power regime as well power to (process and heating) heat, having thanks to the sector coupling better utilization of the technology and additional revenue streams.

TESTS WITH PCM IN GROUTING OF UTES BOREHOLE HEAT EXCHANGERS

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INTRODUCTION: Within the EU-funded GEOCOND project (Urchueguía and Sanner, 2019), one of the research objectives considered the improvement of short-term heat and cold storage capabilities for UTES (Underground Thermal Energy Storage) applications. While UTES usually is intended for seasonal storage of heat or cold, additional short-term storage requirements nevertheless occur often in practical applications. Examples include heat storage from quickly varying sources like solar thermal or discharge to changing loads in district heating networks.

In ATES (Aquifer Thermal Energy Storage), control of the pump rate can help to adjust to short-term load variations. This option does not exist in BTES (Borehole Thermal Energy Storage), where heat exchange is limited to conductive heat transfer. Here Phase Change Materials (PCM) are seen as a solution, as they can increase storage capacity of a given volume of material, in this case the filling of the borehole annulus. In a combination of quick reactions of the PCM inside the borehole and the slower heat transfer to and from the surrounding ground, the overall storage behaviour of a BTES can be optimized. This energetic advantage of this approach had already been investigated theoretically (e.g. Rabin and Korin, 1996), but not yet with PCM dispersed in the grout matrix. Hence, in the frame of developing new grout formulas, mixtures with inclusion of PCM were devised and tested.

MATERIALS AND METHODS: The development concerned two separate fields of application, with the respective PCM selection. One application is for individual ground source heat pumps (GSHPs) for heating and cooling and is intended to improve cooling efficiency, e.g. after colder nights. The required working temperature here is in the range of 25-35 °C. The other application concerns UTES in district heating, where short-term fluctuations can be smoothed at an elevated temperature. The PCM for this application should have a working temperature within the range of 50-80 °C.

The additional requirement for the material in both cases is the compatibility with the other components of the grout and the retention of the required grout properties (handling and sealing). The PCM thus must be shape-stable in fine grain size, well mixable for good dispersion and low separation, and stable in the alkaline environment of a typical grout. The rheological and mechanical properties as well as the low permeability of the grout must not be deteriorated. Material selections were tested in the laboratory, in a lab-size reproduction of a typical borehole section ("sandbox" experiment), in a field test with reduced borehole depth at the campus of the Universitat Politècnica de València (UPV) in Spain and in a full-size UTES borehole at the RISE facilities in Borås, Sweden.

RESULTS: Early tests in the laboratory allowed to exclude materials that did not prove stable in the presence of other components in the grout (mainly cement and other additives). Also separation by gravity such as segregation while mixing had to be addressed, e.g. by adjusting the viscosity of the grout mixture, while taking into account the needs for handling and pumpability. The resulting grout containing PCM is characterised by quite uniform distribution of the organic PCM particles throughout the cementitious matrix, which results in good interaction between the matrix and the PCM particles, implying good thermal contact as required for substantial energy storage.

ENERSTOCK 2021

Oral lectures

Prototype tests of grout with PCM were done in a “sandbox” of about 1 m³ at the RISE facilities in Stockholm. The ground was simulated by water-saturated sand, and a PE-pipe embedded in grout was installed inside the sand to represent the borehole heat exchanger. A row of sensors recorded the temperature from the wall of the sandbox through the sand and grout to the wall of the PE-pipe. Different types of grout with and without PCM were tested for comparison. When heated water circulated in the pipe, PCM embedded grout shows less temperature increase in comparison with non-PCM grout, moreover, PCM grouts showed a high temperature gradient. This initial behaviour changed after PCM reached the melting temperature (29 °C). When PCM absorbed the heat during phase change (solid to liquid), it could no longer hinder the heat transfer, and the temperature profile approached to that of non-PCM grout, which implies a thermal storage effect.

In two boreholes of about 12 m depth at the UPV campus borehole heat exchangers grouted with different types of PCM were installed, both for the lower temperature range in GSHP-applications (<30 °C). Performance tests were done in a kind of TRT set-up, and first evaluations hint to a thermal effect within the PCM activity range.

In the RISE facilities in Borås, a borehole of 50 m depth was used to test the grout with PCM for the application >50 °C. Several heating and cooling tests were carried out with temperatures up to 70 °C. To achieve this temperature within about one day, a heat injection rate of 210-220 W/m was applied; for comparison, another run was performed with just 130 W/m of heat injection, keeping the temperature at 40 °C, well below the PCM activity range. Simulations are intended to verify the impact of the PCM.

Deeper evaluation of all tests is ongoing in order to quantify the effects encountered, by using numerical simulation of thermal behaviour with or without PCM. We will include some results from that ongoing work in the final presentation.

While the current cost of the PCM would prevent wider application, a thermal effect of short-term heat storage using PCM dispersed in the grout can be seen, and justifies further work on refinement of the grout formulas and cost-reduction of the materials.

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INTEGRATED ENERGY SYSTEMS USING PHASE CHANGE MATERIALS AS STORAGE MEDIUM – EXPERIENCE FROM NORWEGIAN INSTALLATIONS

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Several Norwegian installations using phase change materials (PCM) as storage medium are designed and set in operation recently. PCM are mainly applied to reduce peak cooling demands.

The experiences with the installations vary, but many of the installations seems to have operational problems or are not operating as expected.

An integrated energy system combining PCM storage and borehole thermal energy storage (BTES) at Western Norway University of Applied Sciences, Campus Kronstad in Bergen, was set in operation in 2014. PCM is utilized for peak load for cooling, and consist of four tanks filled with flat ice elements with salt hydrate solutions with melting point above 10 C. The cooling need has been lower than expected and the PCM has seldom been tested for maximum cooling mode (Oestrich, 2005, Topdal, 2005, Henne & Midttømme., 2018, Ure, 2018).

A smaller installation combining BTES and PCM is operating at Sotra west for Bergen. Due to a high cooling demand, organic PCM of paraffine was included for peak-load shaving

PCM are also installed as cold storages for peak load shaving for three installations in Bergen and one in Oslo. Salt hydrate solutions are used as PCM for all these installations. Salt hydrate solution is in addition used a heat storage integrated in the energy system at ZEB Laboratory in Trondheim. (Jacobsen & Andersen, 2018)

A selection of these systems will be presented. Due to Covid19 restrictions several of these energy systems was running in reduced mode in 2020, lowering the need of peak load cooling I

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LONG-TERM PERFORMANCE OF PP-HTR LINERS FOR PIT THERMAL ENERGY STORAGE

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INTRODUCTION: For giga-scale thermal energy storages, polymeric liner materials, currently mainly based on polyethylene, are used as a water barrier. A desired target value for continuous operation is a temperature level of 95°C. Due to the fact, that existing PE liner materials exhibit a limit lifetime of less than 10 years at 95°C, special PP grades have been conceived, developed, implemented and investigated in collaborative projects (SolPol, giga_TES). The main aim of this paper is to evaluate the long-term stability of the PP base polymer and the upgraded and optimized PP material PP-HTR along with the investigation of the long-term behaviour of welding seams.

MATERIALS AND METHODS: The optimized PP-HTR grade is highly stabilized with an additional tailor-made stabilization package. The reference and the optimized PP materials were extruded by AGRU Kunststofftechnik GmbH to 2 mm thick sheets. Furthermore, welding seams were prepared by hot wedge welding varying the temperature systematically. The liner and the welding seams were sliced to 100 µm thick micro-specimen. These specimens were exposed to hot air and characterized as to the tensile strain-at-break. For lifetime estimation, temperature load profiles characteristic for current Danish seasonal storages and a high-temperature version were considered. To deduce lifetime values the temperature load profiles and endurance time values were merged assuming cumulative damages.

MAIN RESULTS OF THE INVESTIGATIONS ARE:

- The novel PP grades outperform conventional polyethylene liner materials currently used for pit storages with a maximum operating temperature of 80°C.
- While for current Danish seasonal storages a lifetime estimate of more than 50 years was deduced even for the reference PP material, the optimized PP-HTR grade allows for of a lifetime of at least 30 years for the high-temperature version with continuous operating temperatures of 95°C.
- The impact of hot wedge temperature on the stabilization and properties of the welding seam is negligible. The ageing behaviour of welded liners on micro-specimen level is comparable to the extruded liner without welding seam.

SUMMARY & OUTLOOK: Due to the unique costs/performance ratio of the novel PP-HTR grade, this material was recently used to realize a 70,000 m³ thermal energy storage close to Copenhagen (DK). The upscaling of PP-HTR from the laboratory to the real environment scale was successfully carried out in close collaboration of AGRU Kunststofftechnik (Austria), G quadrat (Germany) and PGJ Miljo (Denmark) (<https://www.agru.at/en/applications/lining-systems/innovative-geomembrane-for-hot-water-tanks/>). Ongoing and future research work is dealing with the development of a 100% water vapour barrier liner material.

DESIGN AND CONSTRUCTION OF AN ACTIVE LATENT THERMAL ENERGY STORAGE SYSTEM

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INTRODUCTION: The intermittency of solar energy has made necessary the development of thermal energy storage technologies (Thermal Energy Storage, TES). The storage of latent heat (Latent Heat Storage, LHS) allows to increase the thermal energy accumulated by the material of phase change (Phase Change Materials, PCM), with a much lower temperature change in contrast with sensible heat systems. In the LHS method, energy is stored by changing a material's phase at a relatively constant temperature. The use of PCM materials for LHS purposes, however, presents major drawbacks that must be addressed, such as long-term stability of storage properties, low thermal conductivity, phase segregation and subcooling during the process phase change. [1], [2]

Some studies have evaluated different accumulators based on shell-and-tube technologies. Agyenim et al. [3] demonstrated the superior performance of tubes with longitudinal fins, compared to circular finned-tubes and smooth tubes. The importance of natural convection in the melting process of the PCM has also been studied by Yang et al. [4].

Furthermore, some works have studied the heat releasing using active methods. Maruoka et al. [5] tested a rotative heat exchanger and demonstrated the relation between rotation velocity and heat release.

This work reports the design and experimental characterization for a rotative scrapper heat exchanger using paraffin with melting temperature of 44 °C, for latent thermal energy storage purposes.

MATERIALS AND METHODS: An experimental facility is being built in the research building ELDI at Universidad Politécnica de Cartagena (37.6051° N 0.9862° W in Cartagena, Spain). A sketch of the experimental facility is shown in Fig. 1.

Figure 1. Experimental setup. (1) Chiller; (2) Heat transfer fluid tank; (3) Pump; (4) Coriolis Flowmeter; (5) Immersed PT100 sensors; (6) Rotative LHT storage system; (7) Electric heater.

A circulating pump drives the heat transfer fluid (HTF) from the tank to the Rotative LHT storage system. The temperature of the HTF inside the tank is controlled by a chiller. The HTF used is water.

The rotative scrapper heat exchanger has been built to store energy using a PCM. Paraffin RT70HC, with a melting area of 40°C - 44°C is employed as PCM. The PCM container is surrounded by a water jacket for heat transfer purposes.

Moreover, three electric heaters are located in the bottom of the LHT system in order to get the test temperature with high accuracy. And an electric motor is used to control the velocity of the scrapers.

Furthermore, PT100 sensors are installed HTF ports to evaluate the heat transfer in the working prototype during melting and solidification process. In addition, T-type thermocouples are included in the LHT system to study the temperature distribution along the LHT system. On the other hand, the mass flow through the facility is measured by a Coriolis flowmeter.

RESULTS & CONCLUSION: This paper will present the thermal characterisation of the device that currently is on due course. Melting and solidification test will show the relation between heat transfer and rotation velocity in both processes.

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DESIGN ASPECTS FOR LARGE-SCALE PIT THERMAL ENERGY STORAGE

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INTRODUCTION: Modern district heating and cooling (DHC) systems are a vital technology as we transition into a green economy. They enable the coupling of the heating and electricity sectors for increased flexibility of the overall energy system. In smart DHC systems, large-scale thermal energy storages (TES) allow for the integration of high shares of renewable energy sources (RES) including excess electricity from RES, and the optimization of combined heat and power plants (CHP). The International Energy Agency District Heating and Cooling Technology Collaboration Programme (IEA-DHC) in its strategic research agenda include large-scale TES as central elements of future modern DHC systems. Pit Thermal Energy Storages (PTES) offer cost-effective solutions for large-scale applications. They are made of artificial pools filled with storage material and closed by a lid.

MATERIALS AND METHODS: Data and experiences of a number of realised large-scale Pit Thermal Energy Storages (PTES) in Denmark and Germany was collected and evaluated by the authors within the IEA-DHC project 'Integrated Cost-effective Large-scale Thermal Energy Storage for Smart District Heating and Cooling' (IEA DHC Annex XII Project 3). This ranges from design and investment cost data to operational monitoring data and long-term practical experiences from operators. Monitoring data was used to evaluate the technical efficiency of the PTES over several years of operation and to validate a dynamic simulation model. Investment cost, design data and practical long-term experiences enabled investigations on economic optimisation of design and reliability.

RESULTS: The paper presents results on and discusses the following aspects:

- Typical application cases
- Design concepts, including cost-optimal geometries
- Cost analysis of realized projects and cost functions for the development of future projects
- Validation of a selected PTES simulation model applicable for dynamic system simulations
- Overview of built DHC projects and main experiences

CONCLUSIONS: PTES offer cost-effective solutions for large-scale applications. Where applicable, these TES types have a significant cost advantage compared to conventional heat stores like e.g. above-ground steel tanks. Cost levels of less than 50 €/m³ have been reached and are particularly interesting for DHC applications with a low number of storage cycles (e.g. long-term or seasonal storage of cold or heat).

UTILISATION OF ICE STORAGE SYSTEMS IN SLOVENIA

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Due to the advanced development of mankind on earth, the impact on the environment has also increased over the years. We are witnessing a change in the atmosphere, more and more frequent and pronounced climatic conditions, which we are not used to in individual parts of the world, such as melting of the ice, global warming, various natural disasters etc. With the development of technologies, we must consider the impact on the environment, that we reach for cleaner forms of energy to meet people's needs and, if possible, that we use this energy as rationally as possible. One such area is also the storage of various forms of energy.

According to the storage mechanism, thermal energy storage (TES) is divided into three types: sensible, latent and thermo-chemical storage. Latent heat is the heat that determines the change of phase (transition from solid to liquid or from liquid to gaseous) in the material that stores heat without or little changing of the temperature of the storage medium. Of all the cold storage technologies available, ice storage is the most popular in recent decades due to its high latent heat, especially when available space is limited. The efficiency of such systems was first recognized decades ago in the United States, where these systems are most numerous, and soon in Europe as well. They were the first to install such systems in Switzerland, where they are known for their economical handling and make the best use of their natural resources (electricity obtained from hydroelectric power plants) in both light and dark parts of the day. In Slovenia, systems with ice banks began to appear in the 1990s, and with the increase in the price of electricity and problems with the availability of electricity at the location of facilities after 2000.

With systems with ice banks, cooling energy is accumulated in the form of ice at night with cheaper electricity, and during the day, when the need for cold is high, it is obtained from storage by melting ice. This achieves greater availability of cooling energy, greater system reliability, cheaper operation as well as lower connected power of devices to the electricity grid. We avoid expensive peak electricity, relieve electricity consumption at the peak of the day, and at the same time equalize day and night electricity consumption, which is favorable for both electricity distribution and electricity production.

In Slovenia, the technology of ice banks is being applied more and more often. Among other buildings, this technology is also used by Cankarjev dom, which has a system with nine ice banks for its needs. Cankarjev dom is cultural and congress Centre which presents, produces, co-produces, organises and provides cultural and artistic, congress and other events, state ceremonies, exhibitions and festivals. The building of the Cankarjev dom congress center is interesting to consider because part of this building is underground. The building has ten floors, of which 7 above ground and three below ground. The transition to ice bank technology has allowed them to cut by half the power of their refrigeration units, while saving money. The article will present the current state of the system and research into the possibilities of improving or upgrading the system. At the time of submitting the abstract, the results of the analyzes have not yet been obtained and are therefore not yet mentioned in this abstract.

ELECTROCHEMICAL DEGRADATION OF CARBON-SUPPORTED GOLD NANOPARTICLES

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INTRODUCTION: Gold nanoparticles have attracted significant attention in electrocatalysis¹, for example, as catalysts for CO₂ reduction² and for hydrogen peroxide production through 2e⁻ oxygen reduction reaction pathway³. Surprisingly, only a few works have dealt with electrochemical degradation of gold catalysts⁴. We present here a thorough study of the electrochemical stability of a commercial Au/C sample tested by an accelerated stress test (AST).

MATERIALS AND METHODS: Commercial Au/C sample with 20% gold loading was purchased from Fuel Cell Store. AST consisted of 10 000 fast voltammetric scans (1 V/s) between 0.58 V and 1.41 V (vs. RHE) in 0.05 M H₂SO₄ electrolyte, with and without addition of chlorides. Loss of gold electrochemical surface area (ESA) was monitored continuously during AST. Identical location TEM (IL-TEM) imaging was performed before and after AST to identify degradation mechanisms. Electrochemical flow cell coupled with ICP-MS (EFC-ICP-MS) was employed to detect the nature of gold dissolution under the applied conditions.

Results: A significant loss of gold ESA occurred during AST and was expectedly increased by the presence of Cl⁻. IL-TEM imaging reveals that the dissolution of gold nanoparticles is the main degradation mechanism under the applied conditions. According to EFC-ICP-MS results, gold dissolves transiently during AST, which means during the reduction of previously formed gold oxide. Therefore, these results open a perspective towards (electro)chemical recycling of Au. Namely, it was shown recently that transient dissolution of Pt can be mimicked by changes between oxidative and reductive potentials on metal by exposure to oxidative and reductive gasses, respectively⁵. This approach is especially interesting, since it can be applied for both conductive and non conductive samples containing gold.

CONCLUSION: In this work, we have demonstrated that degradation of Au/C catalyst occurs during hereby applied AST with the dissolution as the main degradation mechanism. Presence of chlorides significantly promotes dissolution of gold nanoparticles, which is certainly undesirable for the stability. Besides providing information about the stability and degradation mechanisms of gold nanoparticles, this study shows the potential application of (electro)chemical approach⁵ for recycling of gold, especially in the presence of chlorides.

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UNIQUE SOLID CARBONATE-BASED SINGLE ION CONDUCTING BLOCK COPOLYMER FOR HIGH-VOLTAGE LITHIUM METAL BATTERIES

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INTRODUCTION: The pressing demand for long-lasting, high-power portable electronics and the emerging large-scale diffusion of electric vehicles (EVs) and energy storage from renewable sources require batteries improved energy density at reduced cost, along with enhanced cycle life and safety.¹ State of the art Li-ion batteries (LIBs) currently on the market contain liquid electrolytes, which makes it difficult to design flexible cells, being also hazardous in terms of leakage and flammability. Within this context, a variety of solid-state electrolytes have been investigated to date as, in principle, they enable extension of the operating temperature range of a device, also ensuring higher safety even in the case of fire, together with enhanced energy and power densities. Among solid polymer electrolytes (SPEs), a new class, namely “single ion conducting polyelectrolytes” (SICs) has deserved considerable attention.²⁻⁵ SICs are composed of a polymer backbone bearing a covalently bonded anionic functional groups along with a lithium counterion free to move and responsible for ion mobility. Because of their single-ion nature, the lithium transport number values approach unity; this accounts for remarkable benefits to the electrochemical performance, because Li⁺ ions are predominantly engaged in the redox reaction while anions remain relatively inactive. In this work we focus on the development of novel poly[(ionic liquid)-b-(carbonate)] block copolymers with single Li-ion conducting features (Scheme 1), showing greatly enhanced performance towards the state of the art of solid state systems in terms of compatibility with high voltage cathodes (e.g., lithium nickel manganese cobalt oxides - NMC) as well as lithium metal anode and operating at almost theoretical capacity in lab-scale cells.

Scheme 1 Synthetic route for the preparation of different poly(carbonate)-based block copolymers.

MATERIALS AND METHODS: Ring opening polymerization (ROP) has been exploited on trimethylene carbonate (TMC) monomer directly using a RAFT-agent having hydroxyl terminal group as initiator and DBU as catalyst to obtain poly(carbonate)-based macro RAFT precursor, which was further utilized in synthesis of different series of block copolymers comprising lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonyl)-imide (LiMTFSI) and poly(ethylene glycol) methyl ether methacrylate (PEGM) via controlled RAFT polymerization. The obtained ionic block copolymers, named poly(TMC)-b-(poly(PEGM)-r-poly(LiMTFSI)) are yellowish rubber-like materials, which physico-chemical properties were thoroughly investigated by mean DSC, TGA, AFM and rheology characterization techniques. Ionic conductivity (σ) was determined by electrochemical impedance spectroscopy (EIS) while Cyclic voltammetry (CV) was used to define the electrochemical stability window (ESW). The electrochemical behaviour of the SICPEs was evaluated by means of constant-current (galvanostatic) charge/discharge cycling in lithium metal lab-scale cells using lithium iron phosphate (LFP) and NMC catholyte.

RESULTS: The initial series of synthesized copolymer poly(TMC)-b-poly(LiMTFSI) showed limited chain mobility of the copolymer network, likely resulting from the interconnection of two different polymeric blocks both characterized by high T_g. Remarkable enhancement of the ionic conductivity was obtained by the addition of PEGM bearing pendant ethylene oxide side chains. As a result, poly(TMC)-b-(poly(PEGM)-r-poly(LiMTFSI)) copolymers, with different PEGM:LiMTFSI molar ratio, demonstrated more than one order of

magnitude increase of ionic conductivity at 70 °C (i.e., exceeding 10^{-6} S cm⁻¹), but improvements are necessary. The presence of the polycarbonate block clearly influences the ESW and the mechanical properties of the solid electrolyte (up to 5.5 V vs. Li⁺/Li). The calculated t_{Li^+} value of 0.91 is high enough to allow homogeneous lithium plating and stripping, thus preventing the formation and growth of inhomogeneous lithium dendritic structures. This was confirmed by constant current (galvanostatic) reversible plating/stripping tests performed at 70 °C at different current density ranging from 0.025 and 0.5 mA cm⁻². Finally the novel SICP under study was employed for the preparation of LFP and NMC composite cathodes, which were tested in Li metal half cells with Li metal/SICPE/composite cathode configuration at 70 °C. In both cases, we observed Li metal half cell delivering stable and efficient charge/discharge cycling (> 145 mAh g⁻¹) during initial cycling, which corresponds to about 90% of the practical specific capacity output of the commercial LFP and NMC used as active material. Excellent stability and capacity retention was demonstrated upon prolonged cycling, with very limited 2 % specific capacity drop after 10 cycles, and outstanding Coulombic efficiency (CE) approaching 100% during the whole cycling test. Thus, no drastic capacity fade during initial cycling was observed, with a CE exceeding 99% for LFP, while improving cycle-by-cycle (exceeding 95% after 5 cycles) for NMC. Slight overpotential increase was observed when doubling the current rate. This behaviour is due to the clear limitations associated with the internal resistance of the cell, mainly affected by the high intrinsic resistance of polyelectrolyte and the not engineered interface between the binder and active material. Note that optimization in this respect is in progress in our laboratories.

CONCLUSIONS: In the present work, we demonstrate that by the effective design and optimization of poly(carbonate) based unit blocks with poly(ionic liquid) based block it is possible to achieve several advantages from mechanical/morphological point of view: phase separation, truly solid-state, enhanced mechanical properties; and from the electrochemical one: single ion conducting features, high lithium ion transport, high electrochemical stability towards anodic potential, effective prevention of dendrite growth. Remarkably, the proof-of-concept lab-scale solid-state Li-metal cells, assembled with such novel electrolyte and LFP or high voltage NMC-based electrodes at high active material loading, provided excellent performances in terms of high specific capacity output, stability and reversible cycling even up to 4.3 V vs. Li⁺/Li.

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DEVELOPMENT OF A PCM-COMPOSITE FOR THE THERMAL MANAGEMENT OF Li-ION BATTERIES

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INTRODUCTION: For a long lifetime of Li-ion batteries a carefully designed thermal management is needed to prevent temperatures beyond the optimal operation range as well as an inhomogeneous temperature distribution within a battery pack. Both would cause accelerated ageing of the batteries. Phase change materials (PCM) can be used to tackle these challenges. Due to the phase change PCM can store the dissipated thermal power of batteries at an almost constant temperature. During low load and stand-by periods the PCM is regenerated by transferring the stored heat back to the batteries or to the environment. Thus batteries can be kept in an optimal temperature range by a proper selection of the PCM's melting temperature. One of the main challenges is the integration of the PCM into a battery pack without the need of a complex housing and sealing. Further it has to be ensured that the PCM can be swiftly regenerated to ensure a repetitive utilization in subsequent charging/discharging cycles.

MATERIALS & METHODS: During the project Rural-Li a shape stabilized PCM-composite was developed at Fraunhofer ISE for the integration of PCM into a battery module. In this work the development of the composite is presented. For the material development it was decided to integrate the PCM into a curing matrix. Different material mixtures and mass fractions were investigated in order to obtain the highest possible storage capacity and at the same time sufficient mechanical stability. For a proper selection of the PCM, numerical simulations were performed to identify suitable melting temperatures for different ambient temperatures, convection conditions and charging C-rates of the battery. Finally, the performance of the PCM-composite is experimentally investigated. Therefore the batteries are emulated by heating cartridges. As load profile a full charging cycle by a constant current is applied. The performance of the PCM is compared to a convection cooling by a fan. Different loads, ambient temperatures and air velocities are investigated. As performance parameters the temperature reduction by the PCM and the regeneration time are selected.

RESULTS & CONCLUSION: For the composite a microencapsulated PCM is integrated in an epoxy resin with a mass fraction of 70 %. Due to the high capsule fraction a melting enthalpy of 141 J/g is reached. The simulation study reveals the dependency of the optimum melting temperature from the ambient temperature and load scenario. The convection condition has no influence on the optimal melting temperature. Furthermore it has been found that the developed composite can reduce the maximum battery temperature significantly compared to a convective cooling. The experimental investigation showed that the max. temperature of the heating cartridges can be reduced by up to 12.7 K for a charging rate of 3C. Also the temperature homogeneity in the battery module is increased by the composite. Further the fan is essential for the fast regeneration of the PCM. Depending on the ambient temperature and air velocity, the regeneration of the heating cartridges is up to six times faster for a convective cooling compared to application of the PCM-composite. In general the developed PCM-composite offers the following advantages and opportunities. The lifetime of a battery module can be increased by reduced maximum temperatures and higher temperature homogeneity compared to convective cooling. Further the operational safety is increased as the cooling can be temporarily provided by the composite alone if the convective cooling fails. For applications with low ambient temperatures the stored thermal energy of the composite can be transferred back to the batteries and keep them at a sufficient temperature level. Further the composite acts as a battery holder due to its mechanical stability.

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COMPOSITE POLYMER MEMBRANES AS ELECTROLYTES FOR LITHIUM-BASED BATTERIES

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INTRODUCTION: Composite polymer electrolytes (CPEs) including lithium-ion conducting ceramic and polymer materials are promising systems potentially able to combine the high ionic conductivity and transference number of the inorganic phase, with good interfacial contact and process ease due to the soft macromolecular matrix. In this work, we report an easy procedure allowing to obtain homogeneous, flexible, self-standing CPEs with improved interfacial contact with the electrodes and ionic conductivity suitable for practical application.

Materials and methods: Cubic garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) was obtained from Toshiba (Japan). Nasicon-type LTP and Ge-doped LTP were obtained after the thermal treatment of a precursor glass quenched in water or on a metal plate. Polymers, oligomers, initiators and plasticizers were purchased from Sigma Aldrich, dried under vacuum, or distilled to remove moisture, and stored in a Ar-filled glove box. Battery grade lithium salts and ionic liquids were purchased from Solvionic. To obtain the CPEs, the ceramic conductor powder was added to a solution containing the oligomer precursors/polymers, the plasticizer, the lithium salt, and the initiator. The resulting mixture was processed into a film by hot-pressing or using a doctor blade and finally polymerized/crosslinked by a free-radical reaction activated by UV-light or heat. The ionic conductivity was measured by impedance spectroscopy in symmetric cells with stainless steel electrodes in the range from -40 to 80 °C. The electrochemical performance in lab-scale lithium metal cells was evaluated by galvanostatic cycling.

Results: The simple solvent-free processes yield mechanically robust, non-flammable, flexible films acting as safe separating electrolytes. Lab-scale lithium metal cells assembled with the CPEs demonstrated remarkable performance in terms of specific capacity and stability upon prolonged cycling. In particular, the cells could deliver the full gravimetric specific capacity at 0.1C rate, specific discharge capacities up to 115 mAh/g at 1C rate at ambient temperature. Cell operation was also demonstrated below ambient temperature.

CONCLUSION: Composite polymer electrolytes with sufficient ionic conductivity (>0.1 mS/cm at 20 °C) and interfacial compatibility with the electrodes can be easily obtained with a simple and rapid solvent-free procedure, which can be used with a wide range of materials towards high energy and power densities under real operative conditions. The same versatile procedure can be easily tailored to procedure different kind of quasi-solid polymer electrolytes encompassing various nonvolatile liquids and/or solid additives depending on the envisaged application.

EFFECTIVE RADIAL THERMAL CONDUCTIVITY MEASUREMENTS OF CYLINDRIC BATTERY CELLS BASED ON THE HEAT FLOW METER METHOD – A METHOD VALIDATION APPROACH

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INTRODUCTION: Thermal conductivity in the radial direction of cylindrical battery cells is of essential importance for the understanding of the thermal behaviour and thermal management of battery packs. This study focuses on the use of already available measurement devices like the Heat Flow Meter - HFM method to determine this needed thermophysical quantity and outlines a validation experiment designed to assess the applicability of this method.

MATERIALS AND METHODS: A composite from cylindric borosilicate glass rods embedded in a cuboid epoxy resin matrix is used as reference material for the validation experiments. The glass rods with a diameter of 10 mm and a length of approx. 200 mm were prepared in a silicone mould with a base area of approx. 200 x 200 mm, stacked on top of each other in several layers. The epoxy resin was used to fill the cavities between the rods and to ensure flat surfaces of the produced composite cuboid. This cuboid sample was then placed in the NETZSCH HFM 446 device and the effective thermal conductivity in radial direction of the glass rods was determined in a temperature range between -10 °C and 50 °C. Additionally, the specific heat capacity and the thermal conductivity of the used single components, borosilicate glass as well as the epoxy resin, was characterized by the means of Differential Scanning Calorimetry - DSC (NETZSCH DSC 204 F1) and the Laser Flash – LFA (NETZSCH LFA 467) method. Subsequently a Finite Element – FE Model of the composite based on 2D thermal conduction elements was developed, implementing the measured material properties of the borosilicate glass and epoxy resin. Finally, this model is used for temperature field calculations with the boundary conditions given by the previously defined HFM method to calculate the thermal conductivity of the FE Model.

RESULTS: The determined thermal conductivity of the borosilicate glass is between 1,129(66) W m⁻¹K⁻¹ and 1,392(80) W m⁻¹K⁻¹ and for the used epoxy resin between 0,181(14) W m⁻¹K⁻¹ and 0,201(14) W m⁻¹K⁻¹ in a temperature range from -50 °C to 100 °C. The measured effective thermal conductivity of the composite is between 0,761(45) W m⁻¹K⁻¹ and 0,791(63) W m⁻¹K⁻¹ in a temperature range from -10 °C to 50 °C. The heat flow calculation from the FE simulation resulted in a calculated thermal conductivity of 0,913(58) W m⁻¹K⁻¹ to 0,977(57) W m⁻¹K⁻¹ in a temperature range from -10 °C to 50 °C.

DISCUSSION: There are considerable differences with a maximum deviation of 24 % between the measured effective thermal conductivity of the borosilicate epoxy resin composite and the calculated results from the above-mentioned FE model. The reason for this deviation might be due to air bubbles in the epoxy resin matrix of the composite as well as worse contact conditions as modelled in the FE simulation. For all these reasons additional experiments are planned to investigate the influence of the number of borosilicate glass rod layers and reduction of contact imperfections as well as measurements of the borosilicate glass stack in air without epoxy resin matrix.

NUCLEATION BEHAVIOUR IN ORGANIC PCM INVESTIGATED BY MICROSCOPY AND MOLECULAR DYNAMIC SIMULATION

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INTRODUCTION: A fundamental problem hindering the widespread use of phase change material (PCM) applications is often the negative impact of supercooling. Heterogeneous nucleation onto a nucleating agent (NA) mixed into a PCM can lower the effect of supercooling in case the NA shows compatible properties. In order to support the choice of the NA it is important to understand these properties and its effect on the PCM. In the underlying study, the behaviour of different NA in a range of organic PCM has been investigated.

Materials and Methods: The phase change behaviour depends on the NA concentration and temperature of the system. In order to understand this behaviour better, a phase diagram has been prepared for a representative PCM-NA system.

Further two different approaches were chosen in order to visualise the phase change of the PCM-NA system. The state of crystallisation of the PCM and the NA within a given temperature range has been visualised with an optical microscope (SteREO Discovery.V12). The investigated PCM were Dodecane, Octanoic acid, Undecanol, Nonadecane and Tertradecanol. The NA were Octacosane and Polyethylene (Mw=1700)].

To gain further insights into the molecular behaviour of the NA and the PCM during crystallisation, molecular dynamic simulations were performed. The simulated PCM was Octadecane and the NA Octacosane with 1.6 %, 5.2 % and 10 % weight percentage. The initial phase of the system was fluid at 310 K and has been cooled down to 300 K, 280 K or 270 K. The distribution of the PCM and NA molecules have been visualised and compared to a reference system consisting of PCM molecules only.

Results: The optical microscopy showed that for the PCM, to which nucleation Octacosane has a positive effect – Dodecane, Octanoic acid and Undecanol – crystallised needles above the melting point of the PCM still exist. The observed needles melt when the temperature exceeds the liquidus line.

In the scale of the MD simulation, a significant difference in the crystallisation behaviour of the PCM depending on the NA concentration could not be shown. Yet, the results of the MD simulation indicate that the molecules of the NA are evenly distributed within the PCM. Even in case of crystallisation, the molecules of the Octacosane do not build a uniform nucleus, but they integrate in the ordered structure of the Octadecane crystal.

CONCLUSIONS: The results obtained by the microscopic analysis are consistent with the behaviour expected by the PCM-NA phase diagram. Moreover, the distribution of the molecules shown by the MD simulation indicates that the observed needles in the microscopic images consist of a crystal mixture of NA and PCM molecules.

XYLITOL USED AS PHASE CHANGE MATERIAL: NUCLEATION MECHANISMS OF THE OVERCOOLING RUPTURE BY STIRRING

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INTRODUCTION: The implementation of Thermal Energy Storages (TES) on a District Heating (DH) system is a key component to incorporate new intermittent renewable energies. Thanks to its high energy density, latent TES is particularly suitable for DH network buildings substations applications [1] but needs more development. To match the application requirements, Palomo del Barrio et al. [2] identified Sugar Alcohols as promising Phase Change Materials. Xylitol is particularly interesting: its total energy density is 4-5 higher than the density of water (120 kWh.m⁻³), its cost is acceptable (< 3€/kg), it is non-toxic and chemically inert. However, it presents a high and persistent undercooling, forcing to add a nucleation triggering technique to the TES system. Duquesne et al. [3] explored different methods to initiate the crystallization of pure subcooled Xylitol. They identified the use of an airlift reactor as a promising way, assuming that the bubbles suspension created by the airflow constitutes good heterogeneous nucleation sites. The current work studies the nucleation mechanisms of pure Xylitol under agitation and puts forward different conclusions.

MATERIALS AND METHODS: Different triggering methods are tested: by shearing the Xylitol sample in a cone-plate rheometer MCR 300, by stirring it with a propeller in a double-walled glass crystallizer and by bubbling at the bottom of another crystallizer. The rheometer and the double-walled containers allow controlling the temperature of the stirred Xylitol. The beginning of the crystallization is detected by an increase in viscosity for the rheometer and an increase in temperature of the Xylitol for the double-walled crystallizers. Thus, different overcooling degrees and agitation velocity are explored.

RESULTS: No crystallization was observed in the rheometer after several hours at high overcooling degrees (40°C). The first results obtained with the double-walled containers had low reproducibility, from no crystallization observed to the creation of many crystal growth sites in few minutes.

CONCLUSION: These results question the reproducibility of previous works and the current hypothesis of a massive heterogeneous nucleation. From extensive testing a new description of the nucleation mechanisms will be proposed.

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ELECTRIC-FIELD INDUCED CRYSTALLIZATION IN ERYTHRITOL

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INTRODUCTION: In Europe, waste heat recovery (WHR) potential accounts for 19% at medium temperatures (i.e. 100–300°C) of the overall 918 TWh WHR potential of the industrial sector. Thermal energy storage systems, and particularly latent heat thermal energy storage systems (LHTESs), are highly attractive for WHR. At medium temperature, polyols (or sugar alcohols) constitute a group with the most outstanding melting enthalpies, with a good sustainability and reasonable prices. However, they suffer of an important supercooling, they tend to vitrify instead of crystallizing and when crystallization takes place, it usually happens at low rates. All those drawbacks limit their use in a LHTES. Various methods for controlling or reducing polyols supercooling were proposed in previous works and the present study aims to explore a promising approach, proposed by Jankowski et al. (2010), i.e. polyols crystallization driven by electric fields (E-fields). To the best of our knowledge, this approach has only been tested in their work, for erythritol, and further research is needed to understand this technique and extend it to other polyols.

MATERIALS AND METHODS: Different experimental setups were designed to explore distinct approaches to control the crystallization of a polyol (erythritol) using E-fields (power supplies: 2 kW DC, 4000 VA from 15 to 1000 Hz AC; piezoelectric elements). The first step of this work endeavored to reproduce at best the initial study of Jankowski et al.. The second was devoted to the adaptation and test of different devices similar to those found in the literature and generally used to study the crystallization of water or proteins. During this second step, depending of the tested configuration, influence of different parameters was explored, e.g. quantity of product, container form factor (plate, beaker, U-tube), heating system (tubular, hot plate, oil bath), material constituting the electrodes (copper, silver), shape of electrodes (wires, sheets, blocks), ground connection or floating electrode configuration, electrical excitation: AC & DC at different voltage (0 - 500 V) and / or frequency (15 - 1000 Hz), piezoelectric arc (order of kV), duration of the electrical excitation.

RESULTS: Despite a configuration very similar to that described in the work of Jankowski et al., it was not possible to reproduce their results. Surprisingly, those obtained here exhibit a similar degree of supercooling, with higher repeatability, but without the use of electrical excitation. One possible explanation is that the support / electrode / thermocouple assembly acts as a heat sink which leads to an anticipated crystallization. One can also notice that the use of different voltages had not impact on the repeatability of the obtained results. The second step of this work, based on devices developed for the crystallization of water or proteins, did not make it possible to observe the slightest impact of an electric field on crystallization either, in spite of numerous parameters tested.

CONCLUSION: Based on our set of experiments, the use of electric fields does not seem a relevant option to control the polyols crystallization and alternative approaches (e.g. mechanical means, additives, bubbling) should be preferred.

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ESTERS AS PHASE CHANGE MATERIALS FOR LATENT HEAT STORAGE APPLICATIONS: INVESTIGATION AND CONTROL OF THE POLYMORPHIC PHASES

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INTRODUCTION: In view of the global decarbonization measures, an increasing share of intermittent renewable energy sources will be integrated within the energy system. Thermal energy storages have gained increasing attention due to their ability to close the gap between energy supply and demand in a reliable, cost-efficient and environmentally friendly manner. Latent heat storages are particularly attractive due to high energy densities and quasi-isothermal charging and discharging profile. The choice of suitable phase change materials is of crucial importance to the development of efficient latent heat storage systems. Bio-based, long-chained fatty esters and triglycerides are reported to possess interesting melting points and enthalpies of fusion for latent heat storage applications at high temperatures, where not many other organic phase change materials are found. However, they also show a tendency to give rise to different polymorphic forms under different thermal conditions. Thus, understanding the polymorphic behaviour of esters and ways to trigger only the desired crystalline phase is of critical importance to the development of esters and triglycerides as phase change materials for latent heat storage systems applications.

MATERIALS AND METHODS: In this study, the thermal and crystalline behaviour of one fatty ester (Methyl Behenate) and one triglyceride (Tristearin) are investigated. In particular, the effect of different heating/cooling conditions on the formation of polymorphic phases is determined via differential scanning calorimetry, x-ray diffraction, infrared spectroscopy and optical methods (microscopy, custom optical methods).

RESULTS: Several solid-solid transformations can be observed and the effect of different heating rates on the transformations is evaluated. The thermal history of the sample is found to have a significant influence on the polymorphic behaviour, therefore a methodology to overcome it is developed. Synchrotron data as well as kinetic studies are presented together with thermodynamic ones to gain a comprehensive understanding of the polymorphic esters' behaviour.

CONCLUSIONS: Polymorphism can have a significant impact on the thermal behavior and effective properties of many bio-based, organic phase change materials. To ensure their robust utilization in latent storage materials, the effect of experimental conditions and additives to the formation of polymorphic phases needs to be understood and controlled.

VALIDATION OF LAURIC ACID AS PCM: STUDY OF THERMAL DEGRADATION UNDER QUASI-REAL WORKING CONDITIONS

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INTRODUCTION: Lauric acid is a phase change material (PCM) with a low temperature melting point ($T_m=44$ °C) which makes it particularly interesting for energy storage in low temperature applications. Being aware that one of the most critical issues when choosing a PCM is its long-term performance, the thermal degradation kinetics of this fatty acid has been studied in a previous work by means of thermogravimetric (TG) measurements [1]. The main conclusions of this preliminary study were that lauric acid degradation proceeds through two mechanisms, one being associated to its evaporation. According to the isothermal degradation curves, lauric acid would totally disappear after 30 days when kept under N₂ at 50 °C ($T_m+ 5$ °C). However, some preliminary isothermal experiments inside an oven with samples of 2-3 g showed that it did not degrade as fast as predicted by the curves obtained from TG measurements analysis. Therefore, in this work further isothermal tests in oven were carried out for comparing the corresponding kinetic analysis with the resulting from TG measurements. For this purpose the oven described in [2] was used for performing isothermal tests of lauric acid at different temperature levels and for different time durations with samples in the range of grams.

MATERIALS AND METHODS: Isothermal tests were performed under air in a vertical oven with a cylindrical ceramic cavity where the sample is allocated and which allows performing tests under controlled heating rate with stand-by periods. Its upper part was covered with a double-glass trap for condensing the released gases and it was installed inside an extraction hood to ensure that tests were carried out in a secure way. Lauric acid used in this work had >98% purity and was supplied by Sigma-Aldrich. Sample containers were glass vials of 8 ml volume and \varnothing 2 cm and the tested lauric acid mass varied from 1 g to 4 g so that the effect of sample size on the conversion could be evaluated. Isothermal tests lasted for periods of 1 h to 6 h in the temperature range from 140 °C to 200 °C and the heating rate to achieve the target temperature was 5 °C/min. Samples were weighed before and after the tests in a scale with 0.1 mg accuracy. As said above, evaporation is expected to be one of the degradation processes occurring upon lauric acid melting. The evaporation rate of a liquid from its free surface is usually described by the Hertz-Knudsen equation but it can also be studied from a chemical kinetics approach [3]. In such case evaporation rate is expressed by Eq. 1: $r_{eva} = -dn_{liq}/Sdt = [(p_{eq} - p)/(2\pi MRT)^{1/2}] \exp(-E_{con}/RT)$ in [mol/m²s], where n_{liq} is the moles of liquid, S is the sample free surface, p is the partial pressure of the liquid, p_{eq} is the equilibrium pressure calculated with Antoine equation, M is the molecular weight and E_{con} is the activation energy for the condensation process. On the other hand, some authors have considered that evaporation is a first order mechanism [4] for which reaction rate is expressed by Eq. 2: $r_{FO} = -d\alpha/dt = A \exp(-E/RT)$ in [1/s] where A is the pre-exponential factor, E is the activation energy of the process and α is the conversion calculated as: $(m_{end} - m_{ini})/m_{ini}$. If we combine both equations we obtain Eq. 3: $d\alpha/dt = r_{eva}MS/m_{ini}$, which indicates that care must be taken when evaporation processes are kinetically evaluated in terms of conversion, since this variable depends on both initial sample mass and its free surface.

RESULTS: The isothermal experiments performed in the oven for the same time duration and different amounts of lauric acid showed that conversion strongly increased as initial sample mass decreased for the same free area, which agrees with Eq. 3. This explains why the kinetic results obtained from TG measurements, which were analyzed in terms of conversion and for which samples in the order of mg are used, predicted a fast degradation of lauric acid [1]. From the isothermal tests performed at various

ENERSTOCK 2021

Oral lectures

temperatures for different times, r_{eva} was calculated for each temperature by plotting n_{liq}/S vs. t (see Eq.1). Then E_{con} was obtained from the slope of the linear plot of $\ln(r_{eva})$ vs. $1/T$. The resulting value was $E_{con}=80,40$ kJ/mol, which is quite close to the value obtained in our previous work [1] for the mechanism associated with the evaporation of lauric acid where the activation energy in air was: $E=77,8$ kJ/mol. Although both activation energy values are almost the same, lauric acid degradation still proceeds much faster in the case of TG experiments than in the experiments done in the oven. This is probably due to different factors like the low amount of sample used in the TG technique or to the ambient pressure, which is not the same in both kinds of experiments.

CONCLUSIONS AND NEXT STEPS:

In this work, isothermal experiments with large amounts of sample have been carried out for studying the degradation kinetics of lauric acid under quasi-real conditions. Since evaporation is one of the degradation processes, it has been observed that the results obtained from TG measurements may not be adequate for predicting the behavior in real working conditions so that experiments with large amounts of material are crucial. In this way the next step is the extrapolation of the kinetic results to the mass range used in real storage applications in order to construct reliable degradation curves for the working temperature range and hence validate the feasibility of lauric acid as PCM.

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COMPATIBILITY OF THE NOVEL Cu-67WT.%Mg PHASE CHANGE MATERIAL IN NON-INERTIAL THERMAL STORAGE APPLICATIONS

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INTRODUCTION: The eutectic composition Cu-66.7 wt.% Mg is of interest as a power and energy dense metallic phase change material suitable for thermal storage applications. The alloy is particularly attractive due to its theoretical compatibility with iron containers. This compatibility is especially relevant for applications which lead to relative motion between the melt and its container, space heating in electric vehicles and as a heat transfer fluid for example. This presentation outlines static and dynamic reaction experiments undertaken at the Institute of Material Physics in Space at the German Aerospace Centre in Cologne. The experiment results are compared to equilibrium predictions and recommendations are made on appropriate container materials for Cu-66.7 wt.% Mg for different applications.

MATERIALS AND METHODS: Cu-66.7wt.% Mg was synthesised in house from Mg rod (99.9%) and Cu shot (99.9%) in an inert gas environment. Static reaction experiments were performed in a purpose-built horizontal reaction furnace. Samples of Cu-66.7wt.% Mg (500-1500 mg) were placed in iron (ARMCO® 99.85%), stainless steel (1.4301) and graphite (<20 ppm ash) crucibles at 550 °C under an argon atmosphere (5.0 purity) for periods of up to 2 weeks. Preliminary dynamic reaction experiments were undertaken for periods up to 3 hours at a relative velocity of 3.1 m/s in an adapted cup and bob rheometer (MCR702, CTD1000) from Anton Paar GmbH. The interfaces between the alloy and crucible/bob were investigated by analysing a prepared cross section with electron microscopy and energy dispersive X-ray spectroscopy.

RESULTS: Iron and graphite were observed to be compatible in static reaction experiments with Cu-66.7wt.% Mg confirming the expected equilibrium behaviour. Chromium was observed to leach from the stainless-steel crucibles and bobs, damaging the surfaces and altering the composition of the melt. Further results from static and dynamic experiments will be presented at the conference.

CONCLUSION: The eutectic composition Cu-66.7 wt.% Mg was shown to be compatible with iron and graphite during long term and dynamic reaction experiments for periods of up to 2 weeks and 3 hours respectively. The alloy appears to be incompatible with stainless steel (304), leaching the chromium from the solid. Cu-66.7 wt.% Mg shows great potential as a thermal storage material in oxygen free, iron contained environments even if they undergo relative motion.

ENERSTOCK 2021

WEDNESDAY, 9 JUNE 2021

SHORT ORAL PRESENTATIONS - POSTER

EFFECT OF RESIDUAL HEAT RECOVERY OF ZEOLITE BOILER IN THERMOCHEMICAL ENERGY STORAGE AND TRANSPORT SYSTEM

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INTRODUCTION: Thermal energy storage and transport system resolving geographical and temporal heat mismatch is one of the technical options to effectively utilize natural local resources to achieve the sustainable region. While a sugar mill in one island in Japan consumes residue of sugarcane (bagasse) as the natural local resource to supply their own heat and power demand, concurrently exhausts unused heat at around 200 degrees as the flue gas of bagasse boiler. Thermochemical energy storage and transport system utilizing zeolite steam adsorption/desorption cycle was considered to store unused heat from bagasse and to supply its heat to vicinal industrial heat demands currently consuming imported fossil fuel. For economically sustainable operation, increase in fossil fuel saving at heat discharging side is important. In this study, increase in heat recovery and fuel saving by applying a residual heat recovery at the bottom of heat discharging device is evaluated.

MATERIAL AND METHOD: We have already developed a heat discharging device named Zeolite Boiler employing moving bed and indirect heat exchanging system and confirmed to generate pressurized steam continuously with non-pressurized chamber. Zeolite is supplied from the top and moved downwards driven by gravity. Saturated steam generated by an existing boiler is injected into the chamber and adsorbed by the zeolite. Adsorption heat is generated by the zeolite and is transferred to the supplied water through a heat exchanger. The function of steam generation by adsorption heat more than injection steam reduced the fuel consumption of the existing boiler. After adsorption process, the zeolite is discharged from the bottom of chamber at around 60-80 degrees. Unrecovered sensible heat remaining in the zeolite should be recovered to efficiently use of adsorption heat. The residual heat recovery provided by a secondary heat exchanger is assumed to be settled below the primary heat exchanger and transfers the remaining sensible heat of zeolite to supplied water for the existing boiler. An experimentally validated 1D numerical simulation model solving mass and heat balance of gas, zeolite and water predicted the performance of the Zeolite Boiler with/without the residual heat recovery.

RESULT: The effect of the residual heat recovery on heat recovery rate and fuel saving depends on the scale of existing boilers because the balance of heat capacity of zeolite and supplied water to the secondary heat exchanger determines the total heat recovery amount. When a Zeolite Boiler with 1500 kg/h of zeolite is cooperated with an existing boiler with 1800 kg/h of steam output, discharged zeolite from the bottom of chamber is cooled down to near the inlet water temperature. By applying the residual heat recovery to the Zeolite Boiler, the heat recovery rate and fuel saving are improved by 20 points and 4.5 L/h of heavy oil, respectively.

CONCLUSION: This study examines the effect of applying the residual heat recovery to the Zeolite Boiler in the thermochemical energy storage and transport system. The numerical analysis indicated that the fuel saving and heat recovery rate are attractively improved in the cooperation of full-scale Zeolite Boiler and existing boiler.

NUMERICAL ANALYSIS OF AIR-PCM COMPACT HEAT EXCHANGERS USING RECTANGULAR MINI-TUBES FOR FREE COOLING IN VENTILATION SYSTEMS

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INTRODUCTION: The major obstacle associated with the LTES is the low thermal conductivity of the Phase Change Materials [1]. This results in low charging/discharging power. The unfavorable thermal performance is intensified in cases where air is used as the heat transfer fluid (HTF).

The thermal performance of LTES systems working with air has been addressed in some research [2–5]. Dolado et al. [3], working on a real scale air-PCM heat exchanger, pointed out that the bottleneck of the heat transfer particularly at low air flow rates could be due to the high resistance on the air side. The analysis showed that the system performance was improved with increasing the flow rate of air or decreasing the air channel thickness; however, at the cost of having a higher fan energy consumption.

Vakialtojjar and Saman [2] analyzed a plate encapsulating PCM system working with air and reported that the thermal performance could be improved by decreasing the dimensions of the air channels and the PCM slabs.

This paper presents using of rectangular mini-tubes as a solution to a robust air-PCM storage unit for free cooling application in ventilation systems. Flat mini-tubes have the advantage of a high area to volume ratio, resulting in low hydraulic diameter on the HTF side augmenting the air heat transfer coefficient significantly. This also causes higher heat transfer area on the PCM side enhancing the conductive heat transfer in the phase change process. This innovative solution is capable of delivering thermally enhanced storage units with high storage capacity. Two-dimensional simulations are provided to compare different configurations and orientations of the mini-tubes.

Materials and Methods: Ansys Fluent 19.5 was used to numerically investigate the incorporation of flat mini-tubes into a rectangular duct of 150x150x200 mm³, with air flowing through the tubes and PCM placed in the shell. The laminar air flow was modelled under constant heat flux boundary condition along the tube length and the mean air heat transfer was used in two dimensional simulations of the phase change process within temperature range of 15-30 °C. RT22HC manufactured by Rubitherm was used as PCM. The thermophysical properties of the PCM were measured and used as input to the model. Given a constant total air flow rate, the number of mini-tubes, oriented horizontally and vertically in parallel formations, was varied and the effect on heat transfer rate in charging/discharging and the storage capacity was analyzed.

RESULTS AND CONCLUSION: The results show that, given a fixed total air flow, increasing the number of mini-tubes reduces the air heat transfer coefficient, while the total UA value has an increasing trend. On the other hand, the air pressure drop through the channels reduces significantly by increasing the number of mini-tubes.

The mean power of solidification and melting increases asymptotically meaning as the PCM packing factor decreases by increasing the number of mini-tubes the additional gain in the mean power reduces. This is attributed to a more modest decrease in the phase change time for low packing factors while the storage capacity of the system has decreased to a higher extent in a linear trend. In the solidification process, the mean rate of heat transfer increased by 29% and 34% at packing factors of 82% and 78% with storage capacity reduction of 6% and 11%, as compared to the case with 89% packing factor. On the other hand, in the melting case, the mean power has increased by 34% and 41% at packing factors of 82% and 78%, with respect to 89% packing factor, whereas the stored energy has a decrease of 7% and 11%.

The mean power analysis shows that increasing the number of mini-tubes increases the phase change power in both melting and solidification processes. This is happening as result of increase in the heat transfer surface area and the PCM thickness reduction between the stacked rectangular tubes causing improvement of conductive heat transfer. However, the result shown that for low packing factor a modest improvement in mean power has been achieved. This points out to the fact that decreasing the stacked PCM thickness in between the mini-tubes may not have a large benefit. On the other hand, since relatively long time was needed to complete the phase change around the tips of the tubes, it is predicted that the mean power could be increased drastically by reducing the tips-distance.

In addition, the modest improvement in mean power of phase change has been achieved despite the reduction in the air heat transfer coefficient, as result of increasing the number of tubes given a fixed total air flow rate. Considering the relatively low rate of heat transfer in case of large number of mini-tubes, the total heat transfer process may still be governed by the resistance on the air side. Thus, it is important to further investigate the phase change process for higher flow rates, resulting in higher air heat transfer coefficient. The current two-dimensional simulations may be beneficial to analyze the process and to compare different configuration in a single cross section of the component but in fact the air flow may experience a large temperature change along the length of the mini-tubes. Hence, simulating the process in three dimensions as a future work could be highly valuable in capturing the heat transfer process more appropriately.

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APPLICATION OF MACRO-ENCAPSULATED PCM IN LIGHT WEIGHT BUILDING STRUCTURE FOR REDUCTION OF COOLING ENERGY USE

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INTRODUCTION: Thermally well-insulated lightweight framed buildings prevent heat losses through their envelope and reduce the energy demand over the heating season. However, the heat capacity of the lightweight wall is relatively low and in summer, the building lacks thermal stability and overheats. Since the overheating of modern lightweight prefabricated structures is an increasingly common problem on a global scale, the macro-encapsulated PCM is one of a possible solution for improving thermal comfort and decreasing energy demand for cooling.

METHODOLOGY: Single-family building was investigated with DesignBuilder™ software under three geographical locations - Ljubljana (Slovenia), Rome (Italy) and Copenhagen (Denmark) during the 1st week of August and the entire test reference year (TRY). A lightweight structured building envelope is improved by the addition of the internal layer of macro-encapsulated BioPCM with various melting points (MP) at 23°C, 24°C and 25°C and at PCM with MP at 24°C reduced for half of its thickness. The article presents the effect of the Bio-PCM's presence in the building envelope, the effect of the MP of the PCM and its thickness on the thermal indoor environment in the building. The result analysis is performed based on the mean operative temperature in the zones of the building (T_o) and also on the additional energy needed to cool the building comfortable environment. The upper and lower limits of T_o were defined within Category III of the indoor environment during the cooling season determined in EN15251:2007 - the upper and lower limits for T_o are 27°C and 22°C.

RESULTS: The results showed that in Copenhagen, in all tested cases (including the lightweight structure without PCM) the indoor T_o during the 1st week of August stay within the category's range. In Ljubljana, the application of PCM with MP at 23°C showed almost no effect and the T_o in the three hottest days exceeded the upper limit. The rest of the PCM variations could reduce the highest peaks within the category's range. In Rome, besides the application of PCM with MP at 23°C, the variations can drop the T_o within the category's limits. The results show that the PCM with MP at 24°C (at full and reduced thickness) show the best effect towards decreasing the T_o within the range and thus, improves the thermal comfort and decreases cooling demand at all locations. Consequently, the energy consumption without the application of PCM is the highest in Rome (1.71 kWh/m² for the 1st week of Aug and 56.6 kWh/m².a). The effect of other PCM application was relatively similar with minor deviations (mean values: Ljubljana: 1.3 kWh/m² for the 1st week of Aug and 50.6 kWh/m².a; Copenhagen: 1.1 kWh/m² for the 1st week of Aug and 48.2 kWh/m².a and Rome: 0.91 kWh/m² for the 1st week of Aug and 48.5 kWh/m².a).

CONCLUSIONS: PCM as thermal storage in building envelope was shown as a promising solution worth further investigation. However, its performance depends on many spatial factors that first need to be accessed on a minor scale on the level of the wall intersection.

COMPARATIVE PERFORMANCE AND EFFICIENCY ANALYSIS OF A LATENT HEAT STORAGE USING HDPE OR ERYTHRITOL FOR DEMAND-SIDE MANAGEMENT

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INTRODUCTION: Thermal energy storages using waste heat have a high potential for the use of excess heat which is mostly unused today [1]. Thermal energy storages enable energy savings and the reduction of CO₂ emissions by improving the demand side management and load shifting. Latent heat storages are mostly still under development, whereas sensible water storages are already state of the art. For latent heat storages, applications with temperatures above 373 K are especially interesting due to their high energy density and much lower pressure level than pressurized water storages.

In the temperature range between 373 and 623 K a wide range of phase change materials (PCM) are available. One promising group are organic polymers. Like most PCM, polymers suffer from low thermal conductivity and therefore they have mostly been investigated as form-stable PCM [3] or as encapsulation material [4]. Very few publications focus on their use as storage materials [5] even though they offer very favourable properties for the use as PCM. Most polymers are produced on a large industrial scale, which leads to a high availability and thus low prices for common plastics [5]. One especially interesting polymer is high density polyethylene (HDPE), since it has some major characteristics necessary for storage materials: high phase change enthalpies, low-cost, high stability in molten state, non-toxic and high availability. Its low thermal conductivity can be compensated through storage design. Due to its many advantages, HDPE was chosen as PCM for the newly developed heat storage.

Besides polymers, sugar alcohols have a huge potential as PCM, since they have a suitable melting point in the desired temperature range between 373 and 623 K and a high enthalpy of fusion. They are also non-toxic, environmentally friendly and not corrosive. Since some are used as food additives or in the pharmaceutical sector, they are produced in a large industrial scale and are highly available. [6] Sugar alcohols may show significant subcooling and some show a low cycle stability. One of the most promising polyols due to its high gravimetric energy density is erythritol with a melting point of 391 K, which has been examined for different applications like waste-heat transportation [7] or adsorption chillers [8]. Because of this, erythritol was chosen as the second PCM for the latent heat storage.

MATERIALS AND METHODS: In this work, two different phase change materials are compared using analytical instruments and experiments with the same latent heat storage tank in technical scale. First of all, the phase change enthalpy and temperature are measured by differential scanning calorimetry (DSC). In addition, several other properties like specific heat capacity and density are detected. Afterwards, the materials are measured in a storage tank with 70 L capacity. The storage tank consists of an up-standing cylinder and two registers of corrugated pipes as heat exchanger. Before and after the storage tank, there are volume flow meters, pressure sensors and temperature sensors. Inside the tank, there are 10 different temperature sensors at three different heights and depths to give a detailed overview over the temperature distribution inside the PCM. To find the optimum operating point, several experiments are conducted with each material. Main goal is to gain a high average output temperature during the first 30 minutes of the discharging process.

RESULTS: The optimum operation point is considered to be the point where the average temperature in the first 30 minutes is the highest compared to the melting point and where the output temperature can be held within a range of 30 K below the melting temperature the longest. Both materials easily stay above 373

K for over one hour and therefore fulfill the minimum goal. Besides analyzing the output temperatures and performance of the different materials, the temperature distribution inside the tank is also monitored. Hereby HDPE is showing a very stable profile and a clearly visible phase change. Erythritol is showing a less stable profile, but a clear phase change with minor subcooling. Due to the tank design the output temperature is only little affected. In both cases, the mass and energy balances are calculated and therefore the losses and the degree of efficiency are determined. On the one hand, HDPE has a higher average output temperature due to the higher melting point. On the other hand, the gravimetric energy density of erythritol is much higher which leads to a higher power output. Because of the different densities and viscosities, the materials put different forces on the heat exchanger material during phase change, which affects the stability and the long-term usability of the storage tank.

CONCLUSION: In summary, the functionality of HDPE and erythritol as a PCM in the same technical size latent heat storage has been proofed. The optimum operation point has been found for both materials. The energy balance as well as heat losses and efficiencies have been determined. In the direct comparison, several differences between the materials can be seen and taken into account for further investigations. Both materials show great potential for further use in latent heat storage.

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PRELIMINARY EXPERIMENTAL STUDY OF A LATENT HEAT THERMAL ENERGY STORAGE SYSTEM BASED ON PILLOW PLATE TECHNOLOGY

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INTRODUCTION. Latent heat thermal energy storage (LHTES) using Phase Change Materials (PCM) is a promising alternative to traditional sensible heat storage systems in terms of energy storage density. However, regarding economics, its cost is not yet competitive compared to sensible storage systems. Highly industrialized heat exchangers solutions can aid to mitigate this aspect. Accordingly, a LHTES system based on pillow plate heat exchangers is herein investigated. Pillow plates are already used in various industrial sectors but, to the best of our knowledge, they have been scarcely applied in LHTES systems.

MATERIALS AND METHODS: A laboratory-scale prototype was produced, comprised by four main elements: the pillow plates, the PCM, an outer tank containing the PCM and auxiliary elements. Water was used as heat transfer fluid (HTF), while the selected PCM was a commercial product: RT60 from Rubitherm GmbH. It shows a phase change temperature around 58 °C and an approximate melting enthalpy of 160 kJ/kg. Several charging and discharging experiments were performed. The HTF mass flow rate and the inlet and outlet temperatures of the LHTES system were monitored. As the phase change temperature of RT60 is 58 °C, the charging and discharging HTF temperatures were 65 °C and 50 °C, respectively. The applied operation temperature gap (15 °C) can be considered representative of domestic heating systems.

RESULTS AND CONCLUSION: From the monitored parameters, the energy absorbed and released during the experiments was calculated. The obtained experimental energy storage capacity under the selected operation conditions (50-65 °C) was 34% higher than an equivalent sensible storage tank. The system presents additional benefits, such as versatility and robustness. Regarding economics, the cost of the prototype was 20 times higher than the cost considered competitive for TES systems in domestic applications. However, a performed economic assessment showed that the cost of larger size systems could be close to competitive levels. Further research on production cost optimization is therefore advisable.

EVALUATION OF LATENT HEAT STORAGE INTEGRATION IN A SWEDISH MULTI-FAMILY HEATING SYSTEM

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INTRODUCTION: Thermal energy storage (TES) is a solution to increase system efficiency and reduce system costs by shifting heat and electricity demand. Benefits of load shifting from peak to valley hours on the demand side are that the electricity grid can be unburdened and the indirect CO₂ emissions during on-peak production can potentially be mitigated [1]. Heat pump (HP) coupled with TES as a demand-side heating and load management tool has been increasingly investigated and applied for residential buildings [2]. Besides bringing grid alleviation for the utility side, a well designed and operated HP-TES system can also potentially bring down the house owners' electricity bills for heating through peak load shifting [3]. Designing a proper integration layout of an active TES unit, especially a latent heat thermal energy storage (LHTES) one, with the heat pump and heat distribution systems requires deep understanding of the domestic heating engineering, and the impacts from the peak-load shifting on the energy efficiency, operating costs, and carbon emissions of the heating system must be comprehensively evaluated to reveal the benefits and drawbacks of the integration. Such comprehensive evaluation is however limited in the literature.

MATERIALS AND METHODS: The study investigates the technical, economic and environmental potential of integrating a LHTES unit into a Swedish multi-family heating system consisting of ground-source heat pumps (GSHP) and electric heaters (EH). The studied LHTES utilizes a novel phase change material (PCM) encapsulation design, which is in the shape of an ellipsoid to increase the surface-to-volume ratio and thereby to enhance the heat transfer in the PCM, which in this case is a commercial product based on paraffin melting at around 60°C. The LHTES unit is integrated to the GSHP on the condenser side for charging during valley hours then supplying to the radiators for peak heating with discharging. The LHTES integrated system is benchmarked against a baseline heating system (with no LHTES) with respect to five main indicators: (1) total electric consumption, (2) the GSHP's Weekly Performance Factor (WPF, the ratio of the sum of heat output from the GSHP to the sum of total electric consumption for the week), (3) electric costs, (4) indirect CO₂ emissions related to electric consumption, and (5) fraction of shifted peak load. Furthermore, two new hourly-based electricity price profiles are proposed for an economically feasible LHTES investment; one with zero off-peak electricity price and the other with negative prices as two possible future electricity pricing scenarios envisaged to encourage demand-side load shifting applications. A quasi-steady state model has been successfully built in this paper in MATLAB® R2018b and Simulink® to model energy use in a multi-family building for a heating-season week in 2019 under baseline heating operation (no load shifting) and peak-load shifting operation. An enthalpy method based packed bed model was built to simulate the transient thermal performance of the macro-encapsulated LHTES unit with ellipsoidal capsules, and a performance map of the heat pump working under various rating conditions was generated to simulate the coefficient of performance (COP) and thereby to infer the electricity consumptions under normal operation and storage charging/discharging conditions. Both the LHTES and heat pump models have been validated with experimental results obtained from in-house component testing. A control strategy has been developed for operating the LHTES, based on statistically determined peak and valley hours for electricity prices in Sweden. The LHTES was set to be discharged during peak hours and charged during valley hours to shift the heat load and thereby electricity use.

RESULTS: The results indicate that it is possible to time shift 27% of the peak electricity consumption using the LHTES. The total electricity costs increased by 6.3% with a 7.5% increase in electric consumption from

the GSHP, as a higher condensation temperature is needed for melting the PCM in the charge mode. This is because during the charging hours the condenser water outlet temperature needs to be increased from around 40°C, which equals the supply temperature of the heat distribution system, to 65°C as required heat transfer fluid (HTF) inlet temperature of the LHTES unit to ensure melting of the PCM. The increased electric consumption leads to a drop of the WPF by 3% and an increase in the indirect CO₂ emissions by 5.7% if the average electricity CO₂ profile is accounted for from the end user perspective. With a higher electricity price profile during peak hours, the system operational costs can reach break-even; and with an assumingly negative electricity price during off-peak hours, a payback period of 5 years can be achieved with a 50% subsidy on the PCM investment cost.

CONCLUSION: In this work, a numerical investigation has been performed on a LHTES-integrated space heating system to evaluate its technical, economic, and environmental performance under peak load shifting operation. Comparisons on the system performance between the baseline heating operation and load shifting operation reveal that the necessary increase in the condensation temperature of the heat pump during charging periods can lead to increased electricity consumptions, operating costs, and carbon emissions. The economic benefits with the proposed negative electricity profile call for a new electricity pricing system, as well as possibly subsidies to make storage investments economically feasible. The inevitable increase in GSHP's condensation temperature and electric consumption also highlights the complexity of integrating LHTES into heating systems, the importance of system configuration, choice of PCM and control strategy for the most cost-beneficial operation of the LHTES. Studies on optimizing the system configuration and control strategies will entail in future work.

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DESIGN AND OPTIMIZATION OF CLOSED-SYSTEM THERMOCHEMICAL ENERGY STORAGE WITH SURROGATE MODELS

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INTRODUCTION: Thermochemical Energy Storage (TCS) are is considered a crucial technology to increase the share of Renewable Energy Sources (RES) in the global energy mix. In Closed-System TCS, pure vapour at vacuum pressure is used to hydrate a Thermochemical Material (TCM), while a Heat Transfer Fluid (HTF) is used to retrieve the heat generated by the chemical reaction. Common challenges in the design of closed-system TCS reactors are the low material thermal conductivity and the steadiness of the thermal power output. The aim of this work is to propose a practical design methodology for TCS reactors based on surrogate models and multi-criteria optimization methods.

MATERIALS AND METHODS: We consider a cylindrical reactor with bifurcated fins to enhance heat transfer between the Thermochemical Material (TCM)TCM domain and the HTF. A high-fidelity numerical model is built and a sufficient number of FE simulations are carried out to evaluate the rector performance's sensitivity for a defined design domain. We define metrics for the rector performance evaluation: the reaction advancement is chosen as a metric for the amount of energy discharged, while the standard deviation between the discharged energy profile in time and an ideal linear profile is used for the thermal power output steadiness quantification. Hence, surrogate models, in the shape of polynomial functions, are built to cheaply predict the metrics' values as a function of the selected design variables. The use of surrogate models allows for multi-criteria optimization methods to guide the design of the reactor unit. A case study is performed to show the potential of the proposed methodology and the predicted performance are verified with the high-fidelity model.

RESULTS: Response surfaces are built to explore the reactor performances as a function of the selected design variables. The design trends for the maximization of the amount of energy discharged from the TCM suggests the use of branched fins, in agreement with the typical structures for the optimization of heat conduction problems. On the other hand, the steadiness maximization suggests single fins with no bifurcations, as this configuration mitigates the peak of thermal power output. A case- study is carried out using the desirability method with 0.5 weight for each metric, the comparison of the optimized-design performance with a benchmark shows a $\approx 4\%$ discharged energy increase and $\approx 10\%$ increase in the thermal power output steadiness.

CONCLUSION: In this study, we show that the maximization of the amount of energy discharged and the maximization of the thermal power output steadiness are objectives in competition when dealing with the TCS rector design optimization. The use of multi-objective optimization methods is shown as a key for the design of efficient TCS reactors units and the benefits to the reactor's performance are demonstrated by the comparison with a benchmark.

HYBRID STORAGE SYSTEM TO INCREASE SELF-CONSUMPTION OF BUILDINGS

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INTRODUCTION: Due to their considerable flexibility and balancing potential, storage systems will play an important role in the integration of renewable energy sources in the future. The heating sector accounts for around 50% of Austria's final energy demand and around 60% of it is still covered by fossil fuels. Therefore, there is huge potential to increase the share of renewable energy in the heat sector. Renewable heat and electricity sources tend to be fluctuating and often unpredictable and therefore difficult to utilise effectively without introducing storage components. It is generally known that hybrid storage solutions (both electricity and heat) are necessary to introduce a degree of flexibility in buildings and to bridge the gap between supply and demand. For this reason, various technologies for storage and conversion of heat and electricity are being developed and installed in households to reduce their dependency on heating, electrical or gas grids.

METHOD: A new system concept is developed which combines different storage technologies (electrical and heat) to efficiently increase the self-consumption of locally produced renewable electricity and to provide domestic electricity, domestic hot water and space heating for buildings. The innovative concept combined with a sophisticated control for the entire building energy system enable an optimal usage of the different technologies with regard to efficiency and costs by including market signals in the control to make a higher profit by offering flexibility to the electricity grid and therefore have an earlier amortization of the investment costs.

Storage technologies in use:

- i) Redox-Heat Battery: new storage technology based on redox reaction of metals enabling a loss-free storage with 10 times higher energy density compared to water storage. The charging of the storage is by reduction of the metal oxide via hydrogen (produced by hydrolyser driven by renewable electricity) and the discharging of the storage is by reaction with oxygen from the air. (mid to long term)
- ii) Up-cycled second-life lithium-ion batteries still containing 80 % of capacity after 10 years of usage and possible purchase at much lower costs. (short term)
- iii) Thermal heat pump and buffer combination (short term)

The system concept will be proven by a demonstration system integrated in a building complex with combined residential and office buildings in Gleisdorf, Austria.

RESULTS: Preliminary studies expect that the reduction in energy taken from the grids could be up to 30% for the Austrian future system in comparison to the reference cases.

CONCLUSION: Hybrid storage systems have the potential to significantly increase the self-consumption of locally produced renewable energy. The output of the project show that in principle the bigger the building and higher the demand, the more stable the demand requirement is and hence, the prediction is more accurate than for a small building with higher fluctuations. In addition, broaden the focus to two sectors, namely heat and electricity, also enables a more stable operation. The combination of different storage technologies proves that the advantages of each technology can be used optimally and synergies between the technologies can be used to operate the system in an optimal way. To optimize the gains an intelligent control is necessary, which is able to predict the demand side as well as the production side to find an optimal operation strategy.

RELEVANCE OF THERMOCHEMICAL STORAGE IN TES FIELD: A BIBLIOMETRIC STUDY

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INTRODUCTION: Energy storage technologies can provide energy security, fight climate change, and improve the value of current or future energy systems [1]. Thermal Energy Storage (TES) is a key enable technology, it allows to stock thermal energy that can be further used for heating and cooling applications and power generation.

Thermochemical heat is the most promising technology to store thermal energy since the potential it has due to the very high storage capacity. However, this technology is still in at low technology readiness level (TRL) of development and the step forward is taking more time than expected.

This study aims to provide an overview of the thermochemical research within the thermal energy storage field and its technical development, by performing a bibliometric analysis. Therefore, different technology trends and developments, as well as the most productive and influential research can be easily identified. Therefore, the information presented this way, will help everyone involved in TES developments. Regional particularities, policies, financing efforts and economic growth have been evaluated from the point of view of knowledge production. In addition, technological maturity has been observed according to the most dynamic knowledge areas for this specific technology.

BIBLIOMETRICS METHODOLOGY: The methods and tools used to analyze all the literature about the evolution of TCM systems research are described in this section. Bibliometrics is the scientific discipline that studies, in a statistical way, the written publications of certain field of research, and is considered one of the few interdisciplinary research fields that can be extended to almost all scientific fields. Pritchard [2] defined that the main purpose of bibliometric studies is to bring the general picture of the development of a certain research field, as well as the analysis of the leading researchers (authors, journals, institutions and countries) in such area of knowledge. In recent years, many are the studies that have provided a bibliometric overview of their research fields; such are management, econometrics, health economics, marketing, statistics, ecological economics, entrepreneurship, production and operations management, data envelopment, gray systems, and innovation, among others.

To develop the search process, authors have used a search query defined as the main keywords that need to be included or excluded to find the main documents to build the Bibliometric database. The search query is:

""thermochemical "AND ("energy")) NOT ("nano")OR("thermo-chemical" AND ("energy")) NOT ("nano") OR ("TCM" AND ("storage")) NOT ("nano") OR ("sorption" AND ("thermal energy")) NOT ("nano)" in the topic, abstract or keywords sections.

One of the main challenges faced was that, through years, papers that addressed TCM systems did not use the same keywords to refer this technology. The graphics produced following this methodology are:

- Total publications per year
- Total publications per year of the top countries
- Total publications per top 10 countries
- Cumulative publication evolution per country over the last 2 decades
- Cumulative publication of author evolution over the last 2 decades
- Cumulative publication of journal evolution over the last 2 decades
- Total publications per year where they mention the funding

ENERSTOCK 2021

Short oral lectures/posters

- Total publications per year split in three categories those working on materials development, numerical simulations, or system design/development.

RESULTS: The bibliometric analysis results are shown in this section. 8535 papers were accounted (scientific papers and review papers). In general, the evolution follows a growing trend being 2017 the year with higher amount of publication in the field.

Notice that European Union is grouped and is the one that account higher amount of publications in thermochemical heat storage followed by US, China, India, Canada, and Japan.

The cumulative countries evolution over the last two decades regarding the publications in thermochemical field topic.

Europe and USA follow similar trend over the last 20 year in thermochemical field publications and are far away from other countries. However, the evolution of China is highlighted over the last decade, being the growth exponential. Moreover, it is noticeable the role of Japan considering the thermochemical topic since 1999, being one of the top ten countries developing research and technology in this field.

The relevance of the authors working in thermochemical field is highlighted where the cumulative author evolution publication over the last two decades is denoted. Notice that only the top 10 authors are shown in this figure.

The author that published more papers in thermochemical field during the last 20 years was Dr. Aldo Steinfeld. The second more active author in this field was Ibrahim Dincer, followed by Marc A. Rosen.

Moreover, the h index was calculated for each author in this field as a quality indicator of their research. The one with higher h-index is Dr. Donald G. Truhlar which h-index is 43 at this moment considering his publication in thermochemical field followed by Dr. Aldo Steinfeld (h-index=40).

The most relevant journals in thermochemical field are highlighted. The most relevant journal has been Journal of Physical Chemistry A (h index 56 in thermochemical topic) since 2014 when the International Journal of Hydrogen Energy blunt following the same growing trend since 2006. However, the journal with higher impact (higher h-index=57) is Journal of Chemical Physics since the very beginning of the last two decades.

One of the most important parameters to consider in R&D bibliometric analysis is the funding the research has to support its expenses. Therefore, authors that mention their funding source give us the chance to highlight this in a trending bibliometric graph.

Before 2007, almost nobody mentions their funding sources in their publications but this trend is changed in the last years.

CONCLUSIONS: Thermochemical field needs to move forward to reach the market and be spread. The picture from the bibliometric analysis is that the evolution of the field has grown exponentially in importance during the last three decades. However, more deep analysis with bibliometric tool will be done in order to understand and figure out where are the strengths and the weaknesses of the technology. Authors are performing this deep analysis to be presented in 2021 Enerstock conference..

NUMERICAL ANALYSIS OF COMBINED HEAT PUMP ICE ENERGY STORAGE SYSTEMS TO UTILIZE WASTE HEAT ARISING IN NONRESIDENTIAL BUILDINGS

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INTRODUCTION: Since nonresidential buildings (NRB) are often characterized by a high heat and cold demand occurring with a time discrepancy, storage systems increasingly gain attention. Ice energy storage systems (ICES) as an interface between that fluctuating heat and cold demand are a promising technology to utilize waste heat arising inside the building. Several studies examine the suitability of ICES for residential buildings in combination with solar thermal power. However, investigations of system performance regarding plant dimensioning and operation modes for NRB without solar benefit and the possibility to use waste heat are missing. For that kind of system various options of operation modes and energy source management are conceivable, especially regarding mid and long-term optimization. For evaluation and optimization of such an application, analyses of the system behavior via variational calculus are essential. This requires an adjustable model for a large-scale ICES that is convenient for system simulation. Since the operation of the ICES has an impact on the whole supply system, the overall system has to be considered. Thus, an identification concerning the impacts of different operation modes and plant dimension regarding different optimization parameters like economy, ecology and energy efficiency can be carried out. The key challenge is to find a way how it is possible to achieve an increase of energy efficiency and thereby a decrease of CO₂ emission at simultaneous cost reduction.

APPLICATION AND MODEL: To tackle the outlined tasks, in this work a numerical model is developed and its behavior is compared to a 500 m³ ICES located at the Center of Energy Technology (University of Bayreuth). For a characterization, various temperature sensors are utilized to record a height-dependent temperature profile at several positions inside the storage. A radar sensor for determining the degree of icing and volume flow as well as temperature sensors at the in- and outlet are installed. Moreover, for a detailed identification of the consequences on the overall system the data of the whole consumer and producer areas are recorded in a high resolution. Here, the storage acts as heat source for a heat pump (106 kW) that is coupled to the heat distribution of a 5.600 m² research building. Simultaneous and consecutive charging is enabled by a separate heat exchanger connected to the cooling water net. Besides, that net can be directly used as heat source for the heat pump, in periods when the heat and cold demand occur without time discrepancy. Thus, a complete waiving of solar thermal power with its seasonal availability is possible. Beside the ICES, the supply system consists of: a gas fired boiler (500 kW), a gas driven CHP (360 kW), an absorption chiller (280 kW), a compression chiller (800 kW) as well as free cooling (700 kW). That leads to five different operation modes for the ICES and over 900 options for the whole system. The possibility to change set points leads to a further increase of numerous operational strategies. Since the system response is not only a function of the state of charge, a detailed numerical storage model is required to identify an optimal long-term operational strategy as well as an investigation of the influence of plant dimensioning.

VALIDATION: The overall model is set up in MATLAB Simulink, uses various time steps and consists of the ICES as well as the other installed plants. However, for the moment here only the ICES and its periphery are validated. To account for the solid/liquid phase change, an enthalpy method relying on an apparent heat capacity is used. An adjustable discretization in the fluid and in PCM direction is conducted. Furthermore, the quasi 2D model considers i) heat resistance between the heat transfer fluid and the pipe wall, ii) heat conduction (HC) in the pipe, iii) HC in the water and ice, iv) natural convection inside the ICES – which is

ENERSTOCK 2021

Short oral lectures/posters

considered by means of an effective thermal conductivity – as well as v) the coupling to the surrounding ground. In a first step, the implementation of the enthalpy method in the numerical model is validated via the exact solution for the 2-phase Stefan Problem (SP) in cartesian as well as the quasi stationary solution in cylindrical coordinates, with a deviation $< 1.5\%$ for the melt front and temperature profile. In addition, an extensive analysis of the impact of discretization to the deviation compared to the SP and the chosen timestep, which corresponds to the necessary simulation time is performed. Subsequently, a validation with a test rig in lab scale (200 l), that contains several optically accessible pipe sections with identical dimensions as the large-scale storage, is carried out. A connected thermostatic bath enables charging and discharging via separate loops like in the real supply system. By various thermocouples a detailed temperature profile in the storage volume can be observed. Finally, a comparison to the 500 m³ demonstrator shows good agreement. Beside the energy flows from and to the storage also the degree of icing and the temperature distribution inside the storage are compared to the numerically determined results. For the characterization, the targeted discharging started at a specific temperature until no further withdrawal of energy was technically possible by the heat pump and then again heated to the initial condition.

CONCLUSION: A numerical model of an ICES to use waste heat arising inside the building which is suitable for system simulation has been developed. A validation to the exact and quasi stationary solution of the SP shows good agreement. To reflect the behavior of the storage also natural convection inside the storage tank has to be considered. A significant amount of the energy flows can be reduced to gains of the surrounding ground that are also considered in the model. The numerically determined effects of different operational strategies of the whole supply system can prospectively be validated via real plant data by the unique possibility to modify the plant operation. In addition, the adaptable model can be used to identify an optimal storage dimension to cover the real measured demand of a scientific building.

ABSORPTION COLD STORAGE BASED ON PARTIALLY CRYSTALLIZED AQUEOUS LiBr-SOLUTION

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INTRODUCTION: Absorption cooling cycles are well suited to make recovered waste heat or regenerative energy usable for industrial cooling processes. However, energy storage is required to fit these intermittently available regenerative energy or waste heat to continuously running industrial processes. Absorption cooling cycles offer an option to store energy within the operating medium. In absorption cycles, a concentrated salt solution is generated and used in an absorption evaporation process to provide cold, thereby producing a weak solution. Energy storage can be facilitated by storing concentrated and weak solution (and water for evaporative cooling) separately. The energy density strongly depends on the difference in salt mass fraction of the concentrated and the weak solution, which is quite low (about 3-4 m%) in common absorption cooling cycles.

The objective of the presented work was to identify boundaries for the salt mass fraction in both directions, weak and strong, and to calculate resulting maximum energy densities. Furthermore, the technical challenges to approximate the boundaries had to be identified. First economic considerations should decide whether to start further developments.

MATERIAL AND METHODS: The maximum specific energy density has been calculated as a function of the operating temperatures for a lithium bromide solution, H₂O/LiBr, most common in absorption chillers. Thermodynamic equilibrium has been assumed. The upper and lower boundaries of the salt mass fraction have been determined. The difference in salt mass fraction is proportional to the energy density. Approximating the low salt mass fraction boundary, the specific solution mass flow in the absorber has to be reduced significantly. Approximating the high salt mass fraction boundary, partial crystallization of the solution has to be handled. Both boundaries have been explored experimentally. A first economic assessment has been made for a 4 MWh, 500 kW storage using specific component and material costs.

RESULTS: The energy density is 350 kWh/m³, calculated under thermodynamic equilibrium (temperatures 100 °C, 35 °C, 35 °C, 6 °C). The high salt mass fraction of the solution has to be increased up to about 75 m%, consisting of a liquid phase of 65 m% and solid monohydrate of 83 m%. The low salt mass fraction is extended down to 55 m%. The specific absorption capacity per absorber area is thereby reduced to about 50 %. First small-scale experiments (about 200 ml) indicate that a specific cooling capacity of about 800 kW/m³ should be achievable when dissolving the solid phase in discharging mode. The economic assessment determines specific storage costs of about 30 €/kWh.

CONCLUSIONS: The energy density of a partially crystallized H₂O/LiBr storage outnumbers values known from ice storages (90 kWh/m³) or solid sorption energy storages (200 kWh/m³) significantly, even if only about 80 % of the theoretical values could be achieved in praxis. The specific costs are comparable to commercially available ice storages. Therefore, we plan to continue this development.

DEVELOPMENT OF A SENSOR FOR THE DETECTION OF THE CHARGE STATUS OF ICE STORAGES

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INTRODUCTION: As part of the joint project “Sol4City” the Institute for Building Energetics, Thermotechnology and Energy Storage (IGTE) University of Stuttgart (Germany) cooperates with Viessmann Werke GmbH & Co. KG (Germany), AEE INTEC (Austria) and other industrial partners from Austria on the development of integrated solar supply concepts for climate-neutral buildings for the “city of the future”. The innovative concepts further developed by IGTE and Viessmann are based on an energy supply network, also known as a cold district heating network, which serves as a heat source for decentralized heat pumps. In combination with a central, seasonal low-temperature latent storage with water as storage medium and an adaptive and predictive system control, the aim is to realize a highly efficient heating system using solar radiation and environmental heat as main energy sources.

In order to control the heating system, the detection of the store’s charge status is of great importance. At the same time, this detection is a challenge, especially for latent storages such as ice storages, with the solid-liquid phase change due to volume changes and the resulting risk for destruction of the storage tank and/or the heat exchanger. To operate the system in such a way that on the one hand the destruction of the storage tank is prevented and on the other hand its efficiency and use of the storage capacity is maximized, the availability of a sensor for the reliable detection of the charge status of the ice store is essential. As an appropriate sensor is not available up to now the development of such a sensor is a key project goal.

METHODS: State of the art are vertical radar or ultrasonic sensors, which only detect the changing water level in the storage due to the density difference between water and ice. Thus, the state of charge and the amount of ice in the storage cannot be reliably determined [1]. In addition, due to the uneven and asymmetrical icing and de-icing process, these sensors cannot ensure that the storage is protected against destruction at high icing level.

By means of a preceding literature research and the use of an evaluation matrix based on VDI 2222 part 1 [2], in particular sonic rods, horizontal ultrasonic sensors, buoyancy force sensors, sensors for measuring the electrical conductivity and the establishment of an energy balance were identified as the most promising sensor technologies.

Different investigation methods are currently used to develop a suitable charge state detection with the identified sensor technologies. This includes the use of a model ice storage on laboratory scale with which the sensors can be tested for their general suitability. Furthermore, an ice storage with a volume of 12 m³ is used to test the sensors under real operation conditions and for their long-term stability.

OUTLOOK: The aim of the investigations is to develop the most cost-effective and reliable sensor technology for measuring the charge state of ice storages for their reliable operation and prognosis-based system control strategies. In the contribution for the Enerstock Congress 2021, the model ice storage and the real-scale ice storage with 12 m³ volume, newly installed at IGTE, will be described. Furthermore, the working principles of the most promising sensors will be explained and their accuracy and suitability will be compared with the vertical radar or ultrasonic sensors used to date.

ENERSTOCK 2021

Short oral lectures/posters

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EXPERIMENTAL INVESTIGATION OF ZEOLITE PLACED IN A VENTILATION DUCT FOR SPACE HEATING

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The transition to the use of technologies that enable more rational use of energy and obtain it with the least possible impact on the environment is an important topic at the present time, when we are increasingly feeling the effects of climate change. In EU, 40 % of the final energy is used for heating and cooling of buildings. Of this, as much as 75 % is used in residential buildings. It is thus necessary to start using more energy-efficient heating and cooling technologies, optimize their use or provide it from renewable sources. One such technology is heat storage, which allows us to store excess heat or cold at some point in time for later use.

Ever since the global energy crisis in 1970, the need for storage technologies has been growing. According to storage methods, heat storage is divided into latent, sensible and thermo-chemical. With a thermo-chemical storage tank, we need a much smaller storage tank volume to meet the annual energy storage needs, for an energy-efficient passive house, than for the other two types of storage tanks. This was also discovered in our comparison of thermochemical and sensitive seasonal storage tank, according to different collector areas and storage tank volumes, in order to show the percentage of coverage that can be provided. These findings were published in an article entitled: Experimental and numerical analysis of seasonal solar-energy storage in buildings, in International journal of energy research. Thermo-chemical storage includes thermo-chemical reactions and sorption processes, both of which generate energy through heat supply. In thermo-chemical reactions, energy is stored through a reversible reaction, and is consumed when the reaction is reversed. Adsorption is defined as the binding of a gas to the surface of a solid or porous material.

Through research that has already been done in the field of energy storage with the principle of adsorption, it is clear that this field is very promising. The paper presents two experiments in the field of adsorption-based space heating. In the first experiment, measurements were carried out on two adsorbents, zeolite 13X with binder and binder-free zeolite NaY, which were placed into a duct, through which air was transported by means of a centrifugal fan. In the first experiment, the main medium was air to which moisture from humidifier was added, while in the second experiment, only moisture was used as the medium. During the experiments, several different temperatures were measured, duct and fog temperature and the temperatures at different locations in the adsorbent pack in the duct. Experimental results showed that even 134 g of binderless zeolite placed in a ventilation duct heats air to 134°C (peak temperature) which then drops to 25°C in 23 minutes. This shows potential for the use of released heat for purpose of heating with appropriate temperature regulation of outlet air. We found out that adsorption is a promising technology of energy storage for space heating. Additional researches of heat and mass transfer simulation/optimisation as well as material developing/testing are needed.

SIMULATIVE DESIGNING OF THERMAL HIGH PERFORMANCE STORAGEES FOR ELECTRIC BUS HEATING

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INTRODUCTION: Battery electric buses are facing huge challenges when interior heating is required on winter term conditions, since the heating demand can exceed the power that is required for traction. As state-of-the-art solutions for providing interior heating, diesel fueled heaters, electric resistance heaters or electric heat pumps are used. However, when using diesel fueled heaters, local emissions are emitted. When using electric resistance heaters, electric energy from the battery is consumed cutting the range of the vehicle up to more than 50 %. When using heat pumps, overall energy consumption for interior heating is reduced as well as range reduction. However, it is still very significant on cold ambient conditions. Additionally, a second heater has to be used, since the thermal output of available heat pumps is not sufficient on temperatures below -10 °C.

To overcome this challenge, the use of a Thermal High Performance Storage (THS) as stand-alone heating solution or additional heater can be used, as already proposed in past publications. The THS can be electrically charged simultaneously to the traction battery. The stored energy afterwards is used for heating the interior. The benefit of using a THS for interior heating is that no local emissions occur and no energy from the battery has to be used for heating. Compared to currently used batteries, a THS can be up to 90 % cheaper, 50 % lighter and 40 % smaller. To exactly identify these potentials, a simulative designing method is required for designing the optimal THS for the specific use case. The presentation of this designing method and the tools used for this will be shown by the proposed poster.

MATERIALS AND METHODS: To define the goals of how a THS should be optimized, a wide literature review was investigating the topic of electric buses in general. Target of this was to conclude all vehicle related aspects, the use of a THS as heating solution has impact on. To implement simulation models, the environment of Dymola / Modelica is used.

RESULTS: The resulting designing method is of a holistic approach. It considers aspects like the reference scenario, the vehicle type, energy consumptions (heating, traction, production), ecological aspects, economical aspects or charging / discharging rates of the used energy storage systems (battery and THS). By this, the optimization of a THS is done in a way to be optimized for the overall vehicle, not just for the aspect of heating. The implementation of the designing method within the simulation environment of Dymola / Modelica is done in a way, that every partial model can be replaced in future. This allows to use less or more detailed models for any part of the overall simulation model.

CONCLUSION: With the presented designing method of a THS, a step towards maximizing the potential of a THS as heating system in electric buses is done. The holistic approach is highly innovative. By using Dymola / Modelica as simulative environment, linkage with other tools is possible which rises the flexibility simulation tool.

LATENT THERMAL ENERGY STORAGE CHARGING AND DISCHARGING: A NUMERICAL STUDY

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INTRODUCTION: Latent thermal energy storage (LTES) technology has gained significant attention in various solar energy applications by serving as a reserve of energy when solar energy supply and demand are mismatched. In systems utilizing LTES, thermal energy supplied by solar collectors is transported by heat transfer fluid (HTF) and stored inside a phase change material (PCM) during charging (melting) and released during discharging (solidification), utilizing latent heat of the PCM to store and release more thermal energy. Low thermal conductivity is a characteristic of most organic PCMs, so various methods for enhancing LTES thermal performance are suggested and evaluated. Among them, extended surfaces (fins) on the PCM-side of the LTES tank are the most common, with wide variety of configurations; longitudinal, radial (annular and plate), spiral and pin fins being used.

It is the aim of this study to numerically analyze charging and discharging processes in a longitudinally finned shell-and-tube LTES tank, with water serving as HTF and paraffin being used as PCM. Numerical simulations including both phase change processes will be performed neglecting the influence of natural convection in liquid phase of the PCM and the results will be compared with experimental data. The comparison will serve to illustrate the influence of natural convection during melting and solidification of paraffin. Obtained results could be used in further developing of computational models describing melting and solidification processes inside shell-and-tube type LTES.

MATERIALS AND METHODS: Vertically oriented shell-and-tube type tank is used as LTES, containing 19 concentric longitudinally finned tubes. Water, injected at the top into the LTES, flows through the tubes and is used as the HTF, while Rubitherm's RT 25 paraffin is used as the PCM, filling the shell-side.

In order to assess the validity of the computational model, an experimental rig has been set up in the Laboratory for thermal measurements at the University of Rijeka, Faculty of Engineering, consisting of experimental test LTES, water-water heat pump, hot and cold water tanks, three-way mixing valve and circulation pumps. Transient temperature variations of paraffin are measured at three axial and three radial positions at each axial position, around various tubes in the LTES tank, as well as at HTF inlet and outlet positions, with thermocouples used as measurement sensors. They, along with data acquisition system and personal computer, are used to collect and store measurement data. A series of measurements have been carried out for both charging and discharging processes, with different constant values of HTF inlet temperatures and flow rates.

In the numerical investigations, selected computational domain represents the smallest segment of all repeating physical phenomena inside the LTES. Numerical model describes transient three-dimensional fluid flow and heat transfer problem including phase change, which is integrated in the model through the enthalpy formulation. The domain is divided into three subdomains: HTF, tube and fins wall and PCM. A scalar variable in the PCM subdomain is used, representing total (sensible and latent) specific enthalpy, which is coupled with temperature variable on the wall-PCM boundary through a set of user-defined functions (UDFs). Temperatures in the PCM subdomain are obtained from calculated enthalpy values.

Governing equations, consisting of continuity, three momentum and energy equations for the HTF, as well as energy equations for both wall and PCM subdomains, have been solved using the finite volume method according to set initial and boundary conditions. SIMPLE algorithm has been used for pressure-velocity coupling and the pressure correction equation has been discretized through PRESTO! scheme. Discretization of convective terms in momentum and energy equations in HTF subdomain has been performed using

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Short oral lectures/posters

QUICK differencing scheme. Discretization in time has been done fully implicitly, for timestep of 0.1 s. ANSYS Fluent 18.2 has been applied for iterative numerical solving.

RESULTS: Numerical results for both charging and discharging processes have been obtained. Numerically obtained transient temperature variations have been compared against experimentally acquired data. For charging investigations, when PCM melts, the difference between numerical and experimental results increases as the process progresses, clearly showing a growing influence of natural convection in the liquid phase during melting and in molten PCM, and indicating that natural convection in the liquid phase of PCM should be implemented in the model. Results obtained during discharging, when PCM solidifies, are in very good agreement with experimental results, indicating that natural convection has a minor influence on the discharging process. Additionally, temperature and liquid fraction distributions throughout the domain have been presented for both charging and discharging.

CONCLUSION: Charging and discharging processes in a longitudinally finned shell-and-tube type LTES tank, using technical grade RT 25 paraffin as the PCM and water as the HTF, have been numerically studied. Mathematical model, describing unsteady three-dimensional fluid flow and heat transfer, uses the enthalpy formulation for modeling phase change. Natural convection effects in the liquid phase of the PCM have been neglected. Governing equations, with its initial and boundary conditions, have been solved using the finite volume method. From the comparison of numerically obtained transient temperature variations with those obtained through experimental measurements it can be observed that natural convection strongly influences the melting process, since the discrepancy between numerical and experimental results grows progressively. However, the comparison shows small influence of natural convection on the solidification process, since numerical predictions match experimental data quite well. It can be concluded that neglecting natural convection in modeling solidification behavior in longitudinally finned shell-and-tube LTES may be beneficial, since an accurate enough solution could be obtained while significantly reducing computation time. Conclusions drawn from this study can be used in further numerical analyses of charging and discharging, which could be expanded by including natural convection in the model in order to more accurately simulate phase change in longitudinally finned shell-and-tube type LTES.

EXPERIMENTAL INVESTIGATION OF LATENT HEAT STORAGE INTEGRATED ON TOP OF WOOD STOVES

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INTRODUCTION: Wood stoves depend on batch combustion processes yielding a high transient heat production, often reaching higher peak heat outputs than desired by the users. Latent heat storage (LHS), which relies on phase change materials (PCM), comes as a promising solution to this challenge. A compact integrated LHS unit can flatten the wood stoves' peak heat output and prolong it over several hours. A LHS concept has been investigated as a unit to be integrated on top of wood stoves, where a significant share of the heat output could be harvested from the top plate and the stovepipe. The stored heat would then be released to the room, mostly after the combustion ends.

MATERIALS AND METHODS: The concept geometry is based on an annular container, filled with PCM. The experiments use a quarter of the annular container laying on a custom heating plate for finer control of the heat input. High-density polyethylene (HDPE) is used as PCM due to its melting temperature in the range 130-140 °C, its relatively high latent heat and its ability to stand temperatures up to 300 °C without material degradation. Two configurations are tested: (1) with only the PCM in the container and (2) using heat transfer enhancement through metallic rods screwed to the bottom plate. Temperatures are recorded at various locations in the LHS units during 3-6 h charges (melting) and up to 18 hours discharges (solidification).

RESULTS: The melting time is about twice shorter using the specified heat transfer enhancement method. The viscosity of the selected HDPE is insufficiently low to allow free convection to take place and which could have further enhanced the melting process. Even though prolonged over 12-18 hours, the heat transfer to the room during discharge (solidification) is limited and would require additional enhancement features to yield a more substantial thermal output to the room.

CONCLUSION: The experimental results with the LHS concept show that a significant share of the heat output of wood stoves can be harvested and released over a longer time period and yield an overall lower peak heat output to the room. The test results enabled to draw conclusions regarding the design of the next test setup. Additional features will be tested to enhance the heat output to the room during discharge. Alternative HDPE with lower viscosity and eventually higher latent heat will also be investigated.

IMPACT OF TRANSIENT STORAGE TEMPERATURE ON HEAT TRANSPORT SYSTEM DESIGN FOR A THERMAL ENERGY STORAGE UNIT IN VEHICLE APPLICATIONS

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INTRODUCTION: Thermal energy storage units based on metallic Phase Change Materials (mPCM) are a promising potential solution to improve the thermal management of battery electric vehicles. In case thermal energy is needed by a consumer, the storage of thermal energy is potentially cheaper, smaller and lighter than the storage of electric energy. Furthermore, the usage of electric energy from the traction battery for heating goes along with a reduction of vehicle range. Important properties of thermal energy storages in vehicle applications are a high energy and power density, in order to realize a compact design and fast in- and output of heat. Therefore, latent as well as sensible heat of the mPCM is utilized to maximize system performance, leading to a dropping storage temperature over time in heat extraction mode. In this study, the impact of the transient storage temperature on heat transport system design is investigated based on theoretical considerations.

MATERIALS AND METHODS: The storage material considered in this study is the mPCM Al-12wt%Si (melting point 577 °C). Operation storage temperature range investigated is 100 – 600 °C. Resulting heat flux and wall temperature as a function of transient storage temperature, heat extraction rate and overall thermal resistance is studied based on a simple 1-D model.

RESULTS: The results show a big variation of potential heat fluxes from the storage to the heat transport system, indicating the importance of a control concept. High wall temperatures of the heat transport system are found for most of the operation time taking a constant heat extraction rate of 15 W/cm² as a basis. For storage temperatures < 200 °C, the reduction of the thermal resistance plays a vital role in order to achieve the required heat output. It is shown that the transient storage temperature is challenging for an evaporation process because of temporarily high wall overheating and the risk of film and transition boiling. Single phase liquid heat transport is challenging because of the risk of evaporation and high fluid viscosities at lower temperatures in case thermal oils are used. Single phase systems with a gaseous medium show the highest flexibility to a variation in storage temperature, however, are only effective when the process medium pressure is increased and the storage temperature is sufficiently high.

CONCLUSION: It is concluded that the transient storage temperature is a critical boundary condition for heat transport system design. The main challenge is that there is not only a single operation point, but a wide range of operating temperature where the system has to be functional.

REACTIVITY ASSESSMENT OF MAGNESIUM CHLORIDE AND AMMONIA FOR THERMOCHEMICAL ENERGY STORAGE

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INTRODUCTION: The improvement of energy efficiency is a valid approach toward the lowering of global energy demands to reduce the emissions of greenhouse-gases[1]. In the process of energy conversion from primary energy sources to secondary energies, large amounts thermal energy at intermediate temperature (100~200°C) are released into atmosphere. The advanced engineering systems for high-efficiency heat recovery at these temperatures play a crucial role for the realization of future low carbon societies. The thermochemical energy storage (TcES), showing high heat storage density and long-term stability, is a promising choice in the different types of thermal energy storage systems. In the conventional TcES, water reaction-based materials have been examined intensively[2,3]. However, the water-based systems cannot be located in the circumstances at the temperature below water freezing point (~0°C). In this study, we focus on the magnesium chloride/ammonia (MgCl₂/NH₃) system as a new class of materials set for the advanced TcES. This material system works as an efficient heat storage medium with high value of heat output and storage at around 100°C through the reactions with high enthalpy of formation. Furthermore, this system can be utilized in the freezing environment below 0°C without the solidification as the condensation temperature of NH₃ is at -33°C. In addition, MgCl₂ is an affordable and less toxic material. Herein, we demonstrate that the thermal output rates of MgCl₂/NH₃ system can be enhanced upon the cyclic reactions of MgCl₂ with NH₃.

MATERIALS AND METHODS: Magnesium chloride anhydrate (MgCl₂ anhydrate, purity ≥ 98%, Kishida Kagaku Co., Ltd) and ammonia (NH₃, Purity ≥ 99.999%, Showa Denko K.K.) were used as received without further purification. The heat output and storage performances were determined from the variations in sample weight under a flow of NH₃ by using thermal gravimetric analysis (TGA: TGD-9600, Advance RIKO). Surface morphology of the samples were examined by scanning electron microscope (SEM: SM-200, TOPCON Corp.).

RESULTS: The isothermal cyclic NH₃ sorption/desorption tests were conducted to examine the reaction behaviors of MgCl₂ and NH₃ at 100°C. In the sorption process, the partial pressure of NH₃ was held at 1.0 bar, and the desorption process was conducted by switching the flow gas to 100% N₂. Reaction temperature was kept at 100°C in each process. The duration was 30 minutes for both sorption and desorption processes. The results showed that the reactivity in the sorption process was enhanced gradually with increasing the cycle number. The molar ratio of NH₃ adsorbed on MgCl₂ by the sorption processes for 30 min was 1.0 in the 1st cycle and 3.9 in the 5th cycle. Thermal output rate was calculated from the reaction rate in the cycle test. The maximum thermal output rate was enhanced in the cycles by over 10 times from 1st cycle to 5th cycle. The results demonstrate that the reactivity of NH₃ with MgCl₂ was enhanced by the sorption/desorption cycles, a peculiar feature that has not been well-known previously[4]. In addition, the variation of surface morphologies of MgCl₂ anhydrate by the reaction with NH₃ was examined by Scanning Electron Microscope (SEM). It was clarified that the particle grains of MgCl₂ anhydrate with flat and smooth surface were converted into the agglomerates of nanograins after the reaction with NH₃.

CONCLUSION: In this study, the cyclic reactions of MgCl_2 with NH_3 were examined by the evaluation of gas reactivity under isothermal sorption/desorption cycles, and the analyses of morphological variations of MgCl_2 by the sorption of NH_3 . It was confirmed that the reactivity of NH_3 in the sorption process was enhanced gradually with increasing the cycle number in the sorption/desorption cycles. The maximum thermal output rate increased over 10 times from 1st cycle to 5th cycle. Analyses of morphological features clarified that the grains of MgCl_2 anhydrate were converted into the agglomerates of nanograins after the reaction with NH_3 , indicating that the change of the surface morphology led to the enhancement of NH_3 reactivity. We conclude that the $\text{MgCl}_2/\text{NH}_3$ system is a promising materials set to deliver the high performance TcES driving at around 100°C .

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EXPERIMENTAL PERFORMANCE ANALYSIS OF A BENCH-SCALE NH_3 - SrCl_2 THERMOCHEMICAL HEAT STORAGE SYSTEM

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INTRODUCTION: Thermochemical storage (TCS) is one of the most compact type of thermal energy storage (TES), in-addition allowing flexibility in the heat storage/release temperatures. NH_3 -metal halides systems are emerging as TCS materials (TCMs), using metal halides e.g. SrCl_2 , MnCl_2 , CaCl_2 , BaCl_2 , MgCl_2 , and NH_4Cl , [1]-[11]. The authors of this present work have previously numerically designed a bench-scale NH_3 - SrCl_2 TCS system using Aspen Plus [12], [13] and also its reactor-heat exchanger (R-HEX) combined unit using COMSOL [14]. This bench-scale TCS system is now built and commissioned, for ab/desorption of $\text{SrCl}_2 \cdot \text{NH}_3$ / $\text{SrCl}_2 \cdot 8\text{NH}_3$, with two identical reactor- R-HEX units of 0.8 kWh heat storage capacity and 9.4 l volume each, allowing simultaneous heat storage and release. This work aims to evaluate the experimental performance of this TCS system and validate the system's numerical models.

METHODOLOGY: This experimental bench-scale TCS system, for the absorption/desorption of NH_3 to/from $\text{SrCl}_2 \cdot \text{NH}_3$ / $\text{SrCl}_2 \cdot 8\text{NH}_3$, is operated for different temperatures (20-115°C) and pressures (1-10 bar) while measuring the NH_3 flow rates for a number of cycles. These conditions are maintained within the absorption and desorption ranges as per the equilibrium pressure and temperature given by the Van't Hoff expression [15]. The experimental validation of the numerical models of the TCS system [12], [13], and R-Hex unit [14] is conducted by adapting the model components to the real system. A detailed calculation tool in excel was also designed for faster and simpler evaluation of these experimental measurement data. Thereby the key performance indicators (KPIs) such as heat storage/release efficiency, reaction advancement, heat storage/release density and power are evaluated. These experimental KPIs, calculated along mass and energy balances of the system employing the experimental data, also define the system's performance as a TES system.

RESULTS DISCUSSION: This experimental TCS system with the reactor-HEX unit (9.4 l each) can store/release 0.8 kWh heat at each reactor. Using the system's experimental operation for several absorption and desorption cycles, the temperatures, pressures and ammonia flow rates are measured. These data are used to calculate the system's experimental performance in-terms of heat storage/release efficiency during desorption/absorption (as compared to the numerical results of 61% and 67% [13]), as well as the system's heat storage/release capacity and rates. The experimental operation and data acquisition phase of this TCS rig is currently ongoing. The experimental validation and performance analysis of this TCS system enable the design of other TCS systems configurations and indicate the required measures for energy efficiency and charging/discharging rate improvements.

CONCLUSIONS: Upon the experimental validation of the numerical models of the designed and constructed NH_3 - SrCl_2 TCS system, they are proven suitable for scaling-up purposes and design adaptations for other TCS system design configurations. Based on the conducted experimental performance analysis via the defined KPIs, insights are drawn for this kind of TCS systems' design and performance improvements, and the underlying practical aspects as a TES system. This experimental system will also be used for generating bench-scale experimental data of other metal halide-ammonia reactions.

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ELABORATION AND CHARACTERIZATION OF $\text{Li}_4(\text{OH})_3\text{Br}$ -BASED SHAPE STABILIZED COMPOSITES FOR HIGH TEMPERATURE THERMAL ENERGY STORAGE

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The peritectic salt $\text{Li}_4(\text{OH})_3\text{Br}$ is an attractive material for TES application at medium/high temperatures. In this study, this material was thoroughly characterized showing a high enthalpy of reaction of about 250 J/g at 288 °C. It also shows appreciable thermochemical stability with no variation in the phase transition temperature and corresponding enthalpy after 30 heating/cooling cycles. However, like most of inorganic salts, $\text{Li}_4(\text{OH})_3\text{Br}$ is a corrosive material which could limit its application. One of the most efficient solutions to overcome this drawback is the use of shape stabilized composites. It consists of integrating supporting materials to the salt in order to prevent its leakage outside the structure of the composite thus avoiding the direct contact with the container material.

In this study, a simple fabrication method of $\text{Li}_4(\text{OH})_3\text{Br}$ based shape stabilized composites by cold compression, mixing and sintering is presented. Different ceramic materials based on Fe, Cu, Mg, Si, Al, Mn, as micro and nanoparticles were tested. The selection of the optimal supporting material was done based on several criteria, such as i) the chemical compatibility with the peritectic salt which was assessed by differential scanning calorimetry (DSC) and X-ray diffraction analysis; ii) the optimal loading of the supporting material required to afford an excellent structural stability in one hand, and the best storage capacity in the other hand, and iii) the structural and thermal stability over cycling (50cycles) which was assessed by means of differential scanning calorimetry (DSC). The microstructural study of the ss-composite before and after thermal cycling was also carried out by SEM+EDS in order to investigate the morphology and distribution of the salt within the composite and its evolution after multiple cycling. Mg and Fe based ceramics show to be promising candidates for shape stabilization in terms of structural stability (anti-leakage effect), chemical and thermal cycling stability.

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MODELING AND VALIDATION OF THE DEHYDRATION PROCESS FOR THERMOCHEMICAL ENERGY STORAGE USING REACTION RATE EQUATIONS

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Thermochemical Energy Storage (TCES) involves two processes; dehydration and hydration. The literature includes many tests of the dehydration process on the laboratory scale; however, it lacks sufficient and accurate numerical modeling. The reason is that modeling a chemical reaction is in most cases a black box approach since the process is carried out in a certain sequence with many intermediate species develop within. This paper explains how a thermochemical process can be numerically modeled for the dehydration of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ with three reactions involved. The numerical model consists of five different species and the system temperature as variables and is modeled using five species-mass conservation equations and an energy equation. Finite Difference Approach is used to solve the problem along with Matlab as a simulation tool. The model is then validated with the corresponding experimental results and the results show good agreement with the experimental data in terms of species concentrations. On the other hand, the reaction is carried out faster due to the close-to-optimum case assumed in the numerical model, where water vapor is assumed to be momentarily discarded and no reverse reactions are taking place along the process. Comparing the numerical results with available numerical models in the literature, it shows that reaction rate equations are more suitable to model the process than normal conservative equations. The reason of their preference is that they illustrate all intermediate reactions and show all species concentrations developed within precisely.

EVALUATION OF AD/DESORPTION DYNAMICS OF S-PEEK/ZEOLITE COMPOSITE COATINGS BY T-LTJ METHOD

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INTRODUCTION: The transition towards an energy system relying on a mix of energy sources and the consequent widening application of power-to-heat technologies and waste heat recovery call for efficient thermal energy storage systems. Among them, thermochemical heat storage is considered as a viable technology, especially for long-term application. However, its application in full-scale systems has been limited, among the various factors, by the need for performant materials and the possibility to quickly evaluate them for a fast and reliable design of the storage. In this context, the coated reactors present several advantages in terms of heat transfer efficiency. However, a limiting factor on the use of this technology is a low mass transfer due to low porosity and the presence of the binder that reduces the storage performances and could hinder the sorption capabilities of the adsorbent material. In the present paper, a composite material constituted by high zeolite content (up to 90 wt.% of SAPO-34) and sulfonated poly(ether-ether-ketone) (S-PEEK) binder was proposed. The S-PEEK matrix was chosen thanks to its high water vapor permeability, which makes its use potentially effective in this application context. Based on mechanical and thermo-physical tests, this composite coating has shown promising results in terms of mechanical and thermal stability as well as in terms of ad/desorption performances, indicating it as a potential alternative to conventional coatings.

MATERIALS AND METHOD: In order to evaluate its applicability in real conditions, a simplified methodology derived from Large Temperature Jump (LTJ) was used, which was proposed by Aristov et al. [1] and called Thermal Large Temperature Jump; T-LTJ. This method is based on the ΔT measurement at the inlet and outlet of the adsorber due to an abrupt inlet temperature jump. The experimental apparatus is composed of a heating/cooling system and two vacuum chambers separated by a gate valve; one works as an evaporator/condenser and the other is the measuring chamber. In this, the heat exchanger to be tested can be placed and connected to the heating/cooling system that allows the temperature drop/jump in the adsorber in order to generate the isobaric adsorption/desorption.

RESULTS AND CONCLUSION: The measured ΔT , which is related to the heat flux due to the ad/desorption process, was used to study the ad/desorption dynamics with a significantly lower complexity than the other LTJ methods, while still keeping a high reliability. Furthermore, the trend of ΔT can be satisfactorily described by an exponential function whose characteristic time gives an idea of the speed of the ad/desorption process.

Firstly, a comparison test in respect of the reference article [1] was carried out for adsorption process, obtaining comparable values of characteristic time ($134,9 \pm 5$ s vs 116 ± 10 s) and maximal power ($3,4$ W/g vs $3,5$ W/g). Subsequently, the exchanger coated with the composite S-PEEK/Zeolite was analyzed. A characteristic time value of $111,2 \pm 20$ s was obtained, confirming a faster adsorption process associated with an increase in maximal power up to $5,3$ W/g.

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CANADIAN NATURAL ZEOLITES AS STABLE HOST MATRICES FOR LOW-COST, HIGH-PERFORMANCE COMPOSITE THERMOCHEMICAL ENERGY STORAGE MATERIALS

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INTRODUCTION: The commercial availability of low-cost, high-performance thermochemical energy storage materials (TCM) is integral to enabling the widespread deployment of next generation thermal energy storage technology based on physical adsorption and thermochemical reactions. Thermal characterization analysis using a simultaneous thermal analyzer (STA) has shown that Canadian natural zeolites could be suitable host matrices for novel composite TCM at a fraction of the cost of commercially available synthetic zeolites [1]. Additional analysis beyond STA however is required to understand why certain zeolite species possess higher energy storage performance than others. In this study, further investigation in terms of characterization of physicochemical properties and durability testing was conducted to better understand how the unique properties of natural zeolites affect their performance as TCM host matrices.

METHODS AND MATERIALS: Samples of both sedimentary and crystalline zeolites were obtained from ZMM Canada Minerals Corp. (BC, Canada). The screening of these zeolites as suitable TCM was performed with a simultaneous thermal analyzer (Netzsch STA 449 F3 Jupiter) [1]. The structures and surface morphology of the specimens of natural zeolites were examined with scanning electron microscopy (Hitachi S-3400N SEM). Additionally, elemental maps were generated with energy dispersive X-ray spectroscopy (EDX), and a Micromeritics ASAP 2000 analyzer was used to determine surface area, pore size and volume by gas adsorption techniques including the Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. STA was used to measure the thermal performance of the samples over repeated charge and discharge cycles (cyclability).

RESULTS: The results generated from the STA on all the ZMM natural zeolite samples have shown that the High Purity Crystal (HPC) from the TransCanada deposit (Kamloops, BC) possessed the highest water adsorption capacity (0.15 g/g) and the highest enthalpy of hydration (408 J/g). The hydration was performed at 25 °C under 25 mbar of water vapor pressure. Stilbite samples from Nova Scotia displayed the lowest energy storage performance with a water uptake capacity of 0.017 g/g and hydration enthalpy of 35 J/g. The results of the Si/Al ratio and BET analysis of these zeolites coincide with their measured energy storage performances in terms of water uptake and enthalpy of adsorption. High aluminum content points to the high hydrophilicity and better performance of the HPC, whereas lower aluminum content resulted in high hydrophobicity and lower performance of the stilbite. Additionally, the HPC samples were measured to have a BET surface area that is two orders of magnitude greater than that measured for the stilbite samples tested. Preliminary results of repeated charge/discharge cycles using STA have shown that HPC possesses good stability both as a host matrix and as a composite impregnated with calcium chloride.

CONCLUSION: This paper investigates the physicochemical properties of select Canadian natural zeolites from a previous screening study to understand why certain zeolites perform better than others as host matrices for low-cost TCM. Higher BET surface area and aluminum content were characteristic of HPC, which displayed the best energy storage performance in terms of water uptake and heat of adsorption.

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Repeated charge/discharge cycling of samples using STA have shown that HPC is stable as both a host matrix and composite TCM impregnated with calcium chloride.

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PROCESSING SALT-HYDRATES TO THERMOCHEMICAL STORAGE COMPOSITE MATERIALS

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INTRODUCTION: The shift towards renewable heat in domestic buildings is crucial in view of carbon dioxide reduction efforts. Thermochemical heat storages represent a key technology in utilizing solar energy effectively and balance the long term or even seasonal mismatch in demand and supply. Salt-hydrates demonstrate great potential due to high hydration enthalpies and energy densities, however, exhibit instable hydrothermal properties (deliquescence, structural damage upon cycling etc.). As a possible solution the research community moved towards integrating salts in porous materials for structural support [1],[2]. Additional application-side conditions dictate further requirements, such as mechanical stability and suitable temperature range. This work aims to develop composites containing salt-hydrates as alternatives for cost and energy consuming synthetic zeolites. Thus, several well-accessible and low-cost host structures, binders and fiber additives have been combined in effort to stabilize the hydrothermal behavior and to facilitate the handling of the salts for thermal storage applications.

MATERIALS AND METHODS: Salt-hydrates, calcium chloride-CaCl₂ and lithium chloride-LiCl pair, and porous host materials, clinoptilolite and vermiculite, were combined in powder form and processed to spherical granules or cylindrical pellets using hydraulic binders (Portland + sulfate additives). The samples were prepared in disc granulator and extruder, respectively, where main processing parameters were identified and optimized accordingly. The adsorption/hydration properties were analyzed by using the adsorption theory introduced by Dubinin [3]. The relation between the adsorption potential (Gibbs Free Energy ΔF) and corresponding adsorbed mass (or water uptake C , the sorption capacity of the material) known as characteristic curve, was utilized to evaluate the adsorption/hydration behavior. The results were obtained from thermo-gravimetric measurements executed in an open and a closed (evacuated) setup.

RESULTS: Composites with various salt-binder ratios were produced, tested and analyzed. The goal was to establish a balance between favorable adsorption/hydration qualities and applicable mechanical stability, while implementing and maintaining representative industrial processing procedures. Considering the practical case of residential building energy storage for room heating and hot water supply, typical temperatures for adsorption process are defined around 40-60°C at available partial pressure of air humidity in winter around 9 mbar and desorption temperatures of 150-200°C from solar thermal installation at around 6 mbar vapor pressure in summer. These assumptions of adsorption/desorption conditions would translate in values of Gibbs energy of roughly 350-1600 J/g. These limits were used as application boundaries to conduct and evaluate thermo-gravimetric and break-resistance (mechanical stability) measurements. As reference series various mixtures of CaCl₂:LiCl salt-hydrates were impregnated in bulk vermiculite to obtain the main characteristics of selected salt-hydrates mixtures. Further adsorption/hydration behavior of following composites was thoroughly investigated via characteristic curves. Pellets-PS10/50P and granules-PS10/40G, containing 50(9:1) and 40(7:3) wt.% salt, and 10 wt.% PS binder, respectively, yielded promising all-around results. Extrusion method enabled incorporation of higher salt-hydrate content and various fibers in the products compared to granulation method, which improved the water-uptake (adsorbed water vapor mass) in Gibbs energy range of 700 to 1000 J/g. Consequently, the granules show a flat rise in water-uptake during adsorption process from 1600 to 700 J/g following by a steep increase to 350 J/g, compared to pellets, which may indicate a more uniform increase of uptake values from 1300 J/g to 350 J/g. However, the sorption capacity was observed to saturate around 0.2-0.25

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g/g, which are comparable to saturation uptake values of 4A synthetic zeolites. The mechanical stability of the samples was also in the same order of magnitude as zeolite granules considering the lower application boundary of 40°C and 9 mbar (~350 J/g). One of the advantages of developed salt-containing composites is the low desorption temperature around 150°C (at 12 mbar~1200 J/g) compared to e.g. 4A zeolites 250°C (at 12 mbar~2000 J/g). Hence, the latter comparison to 4A zeolites shows, that the characteristic curves of the composites have a steeper slope between 350-1200 J/g Gibbs energy range and reach comparable water-uptake values within narrower temperature range.

CONCLUSION: The stabilization of salt-hydrates in porous host structures in granular and pelletized form for thermal storage applications was the focus of this work. Further enhancement of the composites by extrusion method using fiber additives aiming higher mechanical stability and additional pore-forming purposes, and corresponding effects on adsorption/hydration, is currently being systematically investigated. Hydraulic binders resemble promising supplements for mass production of salt-hydrate composites as thermochemical storage materials. The composites may act as potential low-cost and energy-saving alternatives to zeolites and can be further tuned to suffice specific application requirements.

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TAILORING WATER ADSORPTION CAPACITY OF ALUMINOPHOSPHATE AlPO₄-34

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INTRODUCTION: Microporous aluminophosphate AlPO₄-34 serves as an excellent water adsorbent in thermal energy storage, especially for low temperature thermochemical energy storage. Increasing water adsorption capacity of thermochemical (TCM) material usually leads to higher thermal energy storage capacity, thus offering improved performance of the adsorbent. The main disadvantage of these TCM materials is their high cost due to the use of expensive organic templates acting as structure directing agents. Using ionic liquids as a low cost solvents and structure directing agents can increase the availability of these water adsorbents for TES applications. We present here a green synthesis of AlPO₄-34 large crystals by using imidazole-based ionic liquid.

MATERIALS AND METHODS: The structure of AlPO₄-34 was determined by single crystal XRD. The presence of dimethylimidazolium cation in the micropores was determined with thermogravimetry and IR spectroscopy. Textural properties were determined with nitrogen physisorption. Water adsorption capacity was gravimetrically measured by IGA-100 gravimetric analyser.

RESULTS: The XRD analysis revealed that ionic liquid (33 %), which was used in the ionothermal synthesis, was confined in micropores of large monocrystals. 100 μm monocrystals were obtained at 200 °C after 5 days. Water sorption capacity of AlPO₄-34 material prepared by ionothermal synthesis increased in comparison to the material obtained with hydrothermal synthesis most probably due to the introduction of larger pores during crystallization.

CONCLUSION: Green ionothermal synthesis could be a breakthrough in the low-cost industrial production of aluminophosphate adsorbents, which will provide accessible top-performing water adsorbents for heat storage or heat pump applications.

THERMOCHEMICAL WATER-SORPTION MATERIALS SCREENING FOR THERMAL ENERGY STORAGE: BUILDING APPLICATION

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INTRODUCTION: Thermochemical can be divided into thermochemical with sorption and without sorption [1]. In sorption processes, heat is stored by breaking the bonding force between a sorbent and its sorbate in terms of chemical potential [2][3]. While sorption processes occur at temperatures up to about 350°C, thermochemical without sorption at higher temperatures, higher energy storage densities are involved. Thermochemical with sorption is classified into sub-groups: solid adsorption, liquid absorption, chemical reactions and composites [4]. Chemical reactions are commonly simultaneous chemical/adsorption processes based on the reversible reaction of a solid and a gas and they normally involve a hydration/dehydration reaction (charging/discharging). These reactions are generally assumed to be hydrates with a high number of crystal water molecules (salt hydrates). The most promising candidates according to the literature include [5]: $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ has high stability and good energy density but high-cost and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ has the highest energy density but also is highly corrosive. This research concerns a set of material's characterisation aiming to identify the most promising thermochemical materials for building application. The main relevant parameters and methodology when it comes to select a TCM material is presented. The characterisation methodology considers properties such as energy density, hydration/dehydration conditions, energy density, also volume change and thermal conductivity, which are less studied in the literature.

MATERIALS AND METHODS: Magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, was an analytical reagent grade (CAS: 10034-99-8, MW: 246.48) supplied by Fisher Chemical company©; magnesium chloride, MgCl_2 , was purchased in both anhydrous form from Acros organics (CAS: 7786-30-3, MW: 95.21, Pure) and hexahydrated form from MP Biomedicals© (CAS: 7791-18-6, MW: 203.3, 98%). Potassium carbonate, $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ sesquihydrate, 98.5% purity was supplied by Acros organicsTM (CAS: 6381-79-9, MW: 165.24). Strontium bromide hexahydrate, $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$, (CAS: 7789-53-9, MW: 355.52, 99%), and Calcium chloride hexahydrate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, (CAS: 7774-34-7, MW: 219.8, 98%) both from Sigma Aldrich. Magnesium nitrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.999% trace metals basis (CAS: 13446-18-9, MW: 256.41); Calcium nitrate hexahydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\geq 99.0\%$ (CAS: 13477-34-4, MW: 236.15); Calcium sulphate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, ACS reagent $\geq 98.0\%$ (CAS: 10101-41-4, MW: 172.17); Copper sulphate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, ACS reagent $\geq 98.0\%$ (CAS: 7758-99-8, MW: 249.69); Zinc nitrate hexahydrate and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, reagent grade $\geq 98.0\%$ (CAS: 10196-18-6, MW: 297.49), were all purchased from Sigma Aldrich©.

A simultaneous thermal analysis (STA), STA PT1000 from Linseis, was used to determine whether the thermochemical materials could be hydrated/dehydrated at practical conditions. The STA measurements were conducted from 25 °C to 150 °C at 1 °C/min with an isotherm of 15 min at 150 °C to stabilise dehydration under an air flow of 100 ml/min. The temperature was decreased from 150 °C to 30 °C at 2 °C/min to allow the hydration process. Hydration was performed at 30 °C with a relative humidity of 80% and atmospheric pressure for 2h. The volume variation during dehydration was measured by using a dilatometer from TA instruments, same temperature program and gas flow conditions were applied in this case.

RESULTS AND DISCUSSION: The energy stored was measured at three different heating rates (1 °C/min, 2.5 °C/min and 10 °C/min) up to the operational temperature selected of 150 °C. While some materials are strongly affected by the heating rate (e.g. magnesium chloride and calcium chloride), others do not show

significant differences (e.g. magnesium sulphate and potassium carbonate). The materials that show higher energy density at the lowest heating rate (1 °C/min), in the following decreasing order; magnesium chloride > calcium chloride > magnesium sulphate > strontium bromide > calcium nitrate > zinc nitrate > magnesium nitrate. Potassium carbonate, copper sulphate and calcium sulphate are the ones with the lowest energy density. The specific heat was determined by using the areas and the dynamic method for the TCM hydrated (25 °C) and dehydrated (25°C and 150 °C). The main outputs from this study are that the dynamic method appears to be more accurate than the areas method as the data are the standard deviation is lower and in good agreement with the scattered data in the literature [5]. The thermal diffusivity was measured by the laser flash method for the hydrated and dehydrated TCM form. The thermal diffusivity values of the TCMs range from 0.3 to 0.6 mm²/s, which are also in good agreement with the data reported [6].

CONCLUSIONS: In this work the most relevant salt hydrates candidates from low to medium temperature for building applications have been characterised. Relevant properties such as thermal diffusivity and specific heat capacity, not often characterized in TCM research studies in the literature, have been measured, which provides more experimental evidence for comparison between materials.

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PREPARATION OF PCL BASED SS-PCM AND SHAPING USING 3D PRINTING

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INTRODUCTION: The polyester Polycaprolactone (PCL) is a bio-based polymer that can be processed by the AM technology Fused Deposition Modelling (FDM). In this study, a new method was followed to synthesize SS-PCM, based on the dissolution of the components, in order to increase the weight percent of PCM included in the SS-PCM matrix. PCL was used as a matrix material and RT27 acts as a paraffinic PCM. In addition, the thermal and chemical stability of the blends and the extrusion viability by a 3D printer were evaluated as a proof of concept.

MATERIALS AND METHODOLOGY: Polycaprolactone (PCL) from Sigma Aldrich with a melting point of 60 °C was chosen as a matrix material because it is 3D printable. Paraffin RT27 was used as a PCM, which has a melting point of 27 °C and an enthalpy of 180 J·g⁻¹. Six formulations were prepared with different concentration of paraffin, from 10 wt. % to 60 wt. %. The blends were prepared by the dissolution at 10 wt.% of PCL and RT27 in chloroform separately. Then, to obtain the blends the corresponding ratio of each component were mixed under constant stirring. Finally, the blends were dried in petri capsules for 24 h in an extractor hood. Differential Scanning Calorimetry (DSC) (Mettler Toledo DSC822e) of the base materials and the mixtures was performed to evaluate the enthalpy (ΔH) and the phase change temperature. The test was performed from 15 °C to 80 °C at 1 °C·min⁻¹ with nitrogen flow of 50 ml·min⁻¹. Fourier transformed infrared (FT-IR) spectroscopy coupled with attenuated total reflectance (ATR) (Perkin Elmer Spectrum Two™) was used to evaluate if there is chemical reaction between the matrix and the PCM. The thermal reliability of the different formulations was tested by a thermal-cycling test. Thermal cycles were programmed in a thermal cycler Bioer Gene Q T-18 which allows a tub volume of 0.5 ml and a dynamic method was established following a temperature range between 25 °C and 50 °C and a 5 °C·min⁻¹ heating rate. The thermal stability after 500 cycles was evaluated by DSC and FT-IR. The proof of concept of 3D printing was done with the 3D bioprinter (3D Discovery regenHU). The PCL/RT27 blend is fed into a chamber where it is melted. With compress air and a rotating screw, the material is extruded through a nozzle tip. 110 °C temperature was applied to melt the blends and acquire the proper fluidity. The air pressure used was 3 Bar, the screw velocity was 30 rev·min⁻¹ and the printing rate was 3 mm·s⁻¹. Three different structures were built: woodpile (15x15x2.5 mm), cylinder (90x2.8 mm) and plate (35x12x2 mm).

RESULTS: The thermophysical results of the samples at 0 and 500 cycles are shown in Figure 1. The increase of the RT27 content lead to an increase of the enthalpy in the blend, where the maximum is observed at 60% of RT27 with an enthalpy (ΔH) of 91 J·g⁻¹, at 0 cycles. The melting temperature (T_m) shows a constant trend around 27 °C. The thermal cycled samples present similar values of ΔH and T_m compared to the 0 cycle samples.

The reactivity of the components of PCL/RT27 blends was evaluated by means of the FT-IR. The Figure 2 shows the FT-IR spectra of the blends before and after the 500 thermal cycles. The main bands detected related to PCL are the C-H bonds in the -CH₂ stretching bands (2943-2866 cm⁻¹), the -C=O stretching band (1722 cm⁻¹), the -C-H bond in -CH₂ bending bands (1470-1460 cm⁻¹), the C-O and C-C stretching bands (1293 cm⁻¹), the C-O-C stretching bands (1239-1164 cm⁻¹), the OC-O stretching (1190 cm⁻¹) and -CH₂ rocking bands (760-700 cm⁻¹). The main bands detected related to RT27 paraffin content are the alkyl stretching bands (2956, 2920 and 2851 cm⁻¹) [11]. In the blends samples the functional groups of both materials are detected and no new bands corresponding to new chemical bonds due to a reaction between the two raw materials are observed. Hence, a physical blend is obtained in all the cases. After the thermal cycling, the samples

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show exactly the same bands. The different objects obtained by 3D printing of the PCL/RT27 20% blend. The thermophysical evaluation of the sample after printing was performed, obtaining an enthalpy of $10 \text{ J}\cdot\text{g}^{-1}$ and a T_m around $27 \text{ }^\circ\text{C}$. The enthalpy value is lower than before printing. This could be due to the high temperature used in the printing process that may produce a phase separation inside the extruder because of the high difference of density in liquid state of the different components. As expected, FT-IR shows the same bands as before printing.

CONCLUSION: The synthesis of new SS-PCM based on PCL and RT27 was performed. Six different mixtures with different RT27 content were synthesized. The maximum heat of fusion was observed in the PCL/RT27 60 % wt. blend. A physical blend is obtained without chemical reaction between components in the blends. The stability of the samples was validated after 500 thermal cycles, hence no relevant change of the thermal and chemical properties were obtained after the material characterization. A novel shaping process was used: 3D printing. The thermophysical properties after the 3D printing process are lower in comparison with the original blend properties. In order to improve the performance of the 3D printing processing, more studies are needed to optimize the operation conditions, as well as the use of other polymeric matrixes and AM technologies should be evaluated.

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OVERVIEW ON CSP SYSTEMS AND CURRENT ADVANCED TECHNOLOGIES USED AS STORAGE MEDIA

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INTRODUCTION: Concentrated solar power (CSP) provides a low carbon alternative to generate power from heat to concentrate solar power and produce electricity. To compete with other heat to power technologies, such thermal power plants have to meet the electricity demand round the clock, even if the sun is not shining. Thermal energy storage tackles this challenge by storing heat and providing continuous power over the day producing electricity regardless the time of the day. Thermal energy storage becomes a key element to allow CSP to be highly dispatchable. Different storage technologies have been deployed and investigated over the years since the early 2000s. This work is aimed to give an overview of the storage systems and media deployed for CSP plants applications, demonstrated and/or investigated. Given the importance of TES in CSP, the authors intend to provide a review for technical, policy makers, decision makers and investment audience to address the main technical needs, the reasons of each technology deployment rate, and the future trends and target.

MATERIALS AND METHODS: The technologies studied as TES media are listed in Figure 1 and classified as sensible heat, latent heat and thermochemical heat storage. Such technologies were selected according to expert reports [1], papers [2], and patents related to CSP applications. Each technology was searched in the Web of Science and all the relevant information such as publications, year of publication, country and type of publication was evaluated. The patents were also reviewed through the United States Patent and Trademark Office. All the information was collected and analysed aiming to relate the technical knowledge and the motivation and/or reason that drove each technology to the current TRL (technology readiness level).

Figure 1. TES materials research for use in CSP plants.

Results: There is a gap in the TRL between sensible heat deployment and the other TES technologies (see Figure 2). This study reviews each technology and its deployment separately. For example, while steam generator and molten salts scaled up rapidly to the commercial level in 10 years (TRL 8-9), thermochemical storage after 16 years of research and development at lab and pilot scale, is still at a low TRL level (2-3). Looking at the scientific contributions along the countries, Spain and United States are the countries that have published more on the topic

Figure 2. Scientific contribution over the years and TRL deployment for each technology[3].

Figure 3. CSP implementation and direct normal irradiance in the world from 2006 to 2021. [3].

Figure 3 shows the CSP capacity installed (in operation), under construction, and forecast divided in 4 world zones: North America, South America, South Europe and China. Notice the rapidly CSP growth expected in China for the next years. Since 2011, when the Department of Energy (DOE) launched the SunShot, TES research has targeted more cost-competitive technologies to achieve a CSP power generation price lower than \$15/kWh [4]. The solutions proposed have been focused at material level: increase working temperatures ranges (sensible), novel materials or improve reliability; at system level: new optimized system designs. Future for TES in CSP is still undefined, and innovation is needed. The different TES technologies have to adapt to the CSP operational requirements. Opening the energy market to these new TES-CSP alternatives will increase the penetration of renewable energy into the current energy network and make TES a key enabler in the sector.

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SPEED OF REACHING THE FULL POTENTIAL HEAT CAPACITY OF A BASALT PRODUCT: MATHEMATICAL MODEL BASED ON EXPERIMENTAL RESULTS

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INTRODUCTION: Renewable Energy Sources naturally deliver energy intermittently, causing fluctuations in energy supply. The energy is thus not provided corresponding to the actual need. With the increasing utilization of renewable energy sources, and according to the availability of energy, the demand for energy storage is rising. Energy storages tackle these growing problems and are therefore inevitable for a sustainable energy supply. Carnot-Batteries are one out of a few geographically independent storage possibilities for longer durations. A Carnot-Battery (P2H2P) works in the way that electricity is stored in heat during times of overproduction and reconverted back to electricity when needed. This work focuses on the charging model of a basalt product for packed bed thermal energy storage used in Carnot-Batteries.

MATERIALS AND METHODS: Thermal energy storage tanks for Carnot-Batteries have several variants, like liquid molten salt storage with two-tanks or single-tank thermocline storage and packed bed configurations with encapsulated PCM or natural solid materials like rocks. Storage materials, which are found plenty in nature, having nearly no direct impact on the environment, are water and rocks. Rocks offer a greater temperature span for operation than water and are therefore suitable for a wider range of applications. A possible rock for the use in thermal energy storage is basalt. Basalt is also used in cast form in power plants for flue ash pipes or protective covers of flue pipes, shielding them against abrasion by particles at temperatures up to 550°C. After its usage as a flue pipe, the basalt is a leftover product with changed properties and, so far, no further use. The rock could get the chance for a second life in a Carnot-Battery storage, reducing the impact on the environment even further. To analyse its suitability for such an application, data of this basalt product's energy storage behaviour was collected in prior experiments. This current work depicts the charging model of the basalt product based on these experiments.

RESULTS: The model describes, by partial differential equations, the speed of reaching of heat capacity and charging of the basalt product. It is verified using laboratory experiments.

CONCLUSION: Simultaneously to this steady-state analysis, a second team of researchers is conducting experiments, where the basalt product is analysed in airflow, and preparing a dynamic model of the system. Both studies shall verify the basalt product's suitability as a cheap and environment exonerating energy storage material for Carnot-batteries.

„SYSTEMATIC CHARACTERIZATION OF VARIOUS FILLER CONFIGURATIONS FOR APPLICATION IN MOLTEN SALT UNDER SIMILAR CONDITIONS WITH WATER”

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INTRODUCTION: In order to bring thermal energy storage systems into broad application, costs must be reduced above all. A great opportunity for that is offered by packed-bed storage systems, which consist to a large extent of fillers that replace large fractions of the cost-intensive high-temperature fluids. In order to achieve significant cost savings, the fillers must be inexpensive to purchase and, in addition to their compatibility in contact with the working fluid at the temperature required by the system, they must also have suitable properties to minimize the widening of the thermocline zone. The thickness of the thermocline has a direct influence on the utilization rate of the storage and thus on the specific costs per stored energy. Decisive properties of fillers that determine this expansion of the thermoclines are their shape (surface to volume ratio), size, surface condition, porosity, thermal capacity and thermal conductivity.

MATERIALS AND METHODS: In order to be able to evaluate different filler configurations without the construction of complex prototypes and to be able to pre-select them for a later application, they are systematically studied in a test setup operated with water. Loose bulk of fillers were exposed to a temperature step change from 20°C to 40°C at constant volume flow and temperature of the inflowing fluid in single charging and discharging tests as well as in cyclic operation.

RESULTS: In continuous cyclic operation, a constant temperature gradient at the end of charging and discharging was established after 12 cycles. Experimental results regarding the variation of the properties of the fillers and the resulting quality of the thermal stratification, as the main criterion concerning the suitability of the fillers, will be shown in the oral contribution. As an example for experimental results the charging tests with water and spherical fillers show already a thermocline widening of more than 15 % for fillers with mean diameter of 2.1 cm compared to those with mean diameter of 1.7 cm in case all other parameters of the experimental setup remain constant.

CONCLUSION: Besides operating control of the test system the changes in the size and shape of the filler significantly influence the behavior of the storage tank and the utilization rate. The filler must therefore be carefully chosen.

STEEL SLAG CONCRETE: THERMO-MECHANICAL STABILITY UNDER HIGH-TEMPERATURE CYCLES

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INTRODUCTION: The improvement of the output efficiency in CSP plants is a challenge of major interest. To achieve this objective, an increase of temperature in the heat transfer and the storage media is required to increase power block efficiency. Among the suitable material options, concrete was determined to have attractive properties. Concrete is a heterogeneous material, made of several components that allows to choose the best dosage to obtain the desired properties in the final blender. Worldwide availability of concrete components and their low cost, contribute to implement eco-friendly measures. The environmental impact of the materials is a substantial parameter to take into consideration when selecting concrete components. There are by-products from industries that can be revalorized by including them into concrete mixtures, replacing cement percentage or using them as aggregates. A by-product from the metallurgy industry, known as steel slag or electric arc furnace slag, was previously studied as aggregates in concrete for thermal energy storage. In this paper, the thermal stability under high-temperature cycles, of two cement types with steel slag as the only aggregate in the concrete mixture is compared. As further novelty, the thermal cycles were adapted to heating rates currently used in the operation of a CSP plant.

MATERIALS AND METHODS: In the present study two concrete dosages were designed. One using ordinary Portland cement and the other with calcium aluminate cement. In both binders, steel slag was used as aggregate, considering granulometries of 0-12 mm. Physical, thermal and mechanical properties were studied before and after thermal cycles. To study the thermal stability, 10 continuous thermal cycles were carried out. The thermal cycle profile consisted on a first cycle with a low heating rate 1 °C/min up to 290 °C followed by an isothermal step of 4 hours. Continuously, temperature increased up to 700 °C with the same heating rate and maintaining during 4 hours. After, the samples were cooled down to 290 °C, at a rate below 1 °C/min. For the next cycles the heating rate was increased to 15 °C/min, considering the same time for the isothermal steps and the cooling part.

RESULTS: The external appearance showed a geometry preservation in all samples. There were no important cracks in the surface, only micro-fissures in the samples after some thermal cycles. There is a strong connection between the aggregates and both types of cement paste, conferring a bonding in the concrete mixture. No spalling signs nor thermal expansion of aggregates was observed. The mass loss was around 4 % in both mixtures after the thermal cycles. The thermal conductivity was reduced 50 % after the 10 thermal cycles. Despite the high compressive strength obtained before any thermal treatment, the compressive strength drastically decreased 80 % after the 10 thermal cycles.

CONCLUSIONS: Despite the low thermal conductivity achieved after thermal cycles, a high integrity preservation of the concrete mixtures was observed. The compatibility of steel slag highlight with both cement types conferring a hydraulic bonding to the mixture, appreciating small fissures.

MODELING OF COMBINED CONVECTIVE AND CLOSE-CONTACT MELTING IN A VERTICAL CYLINDRICAL ENCLOSURE

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The use of phase change materials (PCM) for latent heat thermal energy storage (LHTES) and thermal management applications is receiving considerable amount of attention in recent years. During the last decade studies in our lab have discovered that in order to enhance heat transfer during melting process (charging of a storage system), the so called 'close contact melting' (CCM) should be enabled. CCM is possible when there is a hot, usually upward-facing, surface, and the solid PCM is surrounded by liquid PCM or ambient gas medium, and hence can move freely toward the hot surface. Yet, most of the numerical modeling nowadays is done by the 'enthalpy-porosity method' (EPM), a numerical scheme included in commercially-available computational fluid dynamics (CFD) packages that predicts well convective ('regular') melting but is not suitable for the modeling of CCM. In addition, EPM uses an arbitrary constant known as the 'mushy-zone constant', the real physical interpretation of which is still vague.

The main objective of this study is to develop a reliable numerical modeling which combines a general enthalpy formulation for the phase change with a treatment of convective heat transfer and general rigid body motion. Therefore, an advanced numerical model is developed and implemented using an in-house numerical code, built especially for this study. The model was tested vs. known benchmarks from the literature and a good comparison was obtained. The model is then used to perform a parametric study of the contribution of CCM and regular melting to the PCM melting rate.

PCM ABSORBED EXFOLIATED GRAPHITE/POLYMER COMPOSITES FOR THERMAL MANAGEMENT OF LITHIUM-ION BATTERIES

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INTRODUCTION: Electric vehicles are capturing the automobile market slowly and steadily. Call it an improvement over conventional internal combustion engines or one of the steps to arrest global warming; electric vehicles are going to be the next generation vehicles. Electric vehicles run on lithium-ion chemistry. However, these are highly sensitive to temperature and significantly affect the delivered capacity and life span. This leads to battery failure and safety issues such as thermal runaway. Battery Thermal Management Systems (BTMS) are used in electric vehicles to cool down the Lithium-ion battery (LiB). During charging and discharging cycles, the LiB heats up; this increase in temperature reduces the life of batteries. Conventionally, active cooling systems are integrated to overcome the hazards. However, active cooling solutions are not economical, require extra space and moving parts. Phase change material (PCM) based solutions help to maintain the temperature below required temperature, passively. PCM utilizes latent heat to store and release the heat over a narrow temperature range which aids in containing the temperature and its variability. Solid to liquid phase change PCMs experience two major challenges namely material leakage and low thermal conductivity for applying it for BTMS. LiB can also have thermal runaway which leads to fire; hence the composite should also exhibit flame retardant nature.

MATERIALS AND METHODS: In this work, the above challenges of conductivity and flame retardancy have been addressed. Graphite intercalated compound is exfoliated in microwave and liquid PCM is absorbed into graphite matrix. The resultant powder is then thoroughly coated with polymer binder, using conventional coating techniques, and compressed into a block. The study includes effect of size of graphite flakes on percentage of PCM absorption, effect of compaction on thermal properties of the composite.

RESULTS: Further analysis include x-ray diffraction (XRD) for crystallinity and interlayer spacing between two graphite layers. Scanning electron microscope (SEM) is employed to visualize the morphology at each step of fabrication. Latent heat of fusion and phase change behaviour is studied through 3-Layer calorimetry method.

CONCLUSION: Hot disc method is employed to study thermal transport properties. The resultant product makes for an ideal candidate for BTMS.

CONFIGURATION AND STRATEGY OPTIMIZATIONS FOR A NEW DISTRIBUTED ENERGY SYSTEM COMBINING MULTI-ENERGY STORAGE TECHNIQUES

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The combination of distributed energy system and multi-energy storage system has a potential to use renewable energy on a large scale and further improve the system energy efficiency. Therefore, a new type of distributed energy system combining multi-energy storage is proposed in this paper. Its novelty lies in that the three types of energy storage, i.e. cold, heat and electricity are considered simultaneously and the electric vehicle load is also included in the distributed energy system combining multi-energy storage system, which allows the full consideration of the effect of multi-energy storage in the distributed energy system. Two operation modes are proposed to give full play to the advantages of new system according to the charging mode for electric vehicle. Subsequently, a two-layer collaborative optimization method for system configuration and operation optimization is proposed, and applied to a nearly-zero energy community. After that, a two-phase collaborative optimization method is used to explore the operating conditions and economic performance of the new system in nearly-zero energy communities with different proportions of public buildings and residential buildings. The results show that with the increase of the proportion of public buildings, the primary energy saving rate of distributed energy systems combining multi-energy storage increases, but the annual cost savings rate remains basically unchanged. In addition, the hourly operating cost of the distributed energy system combining multi-energy storage is also significantly reduced compared with the separated production system. Therefore, the method of two-layer collaborative optimization in the new system proposed in this paper can be used to realize the optimal system configuration and operation design for energy saving and consumption reduction. Finally, the new system can provide a feasible scheme for the energy supply of nearly-zero energy community in the future.

AN INVESTIGATION INTO THE USE OF BIOMIMETIC DESIGNS FOR IMPROVED EFFICIENCY IN BOTH SOLAR THERMAL AND SOLAR PHOTOVOLTAIC APPLICATIONS.

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INTRODUCTION: With the ever-reducing global dependency on fossil fuels as the primary source of energy, the development of solar energy technologies has accelerated in recent years. Of the many approaches taken in an attempt to discover new methods of increasing the productivity of solar energy devices, one that has gained considerable popularity in recent years is the use of biomimicry in their design; that is, basing the designs of solar energy devices on structures, materials, behaviours, or processes which mimic those of biological organisms. It was such an approach upon which the methodology of this project was based.

MATERIALS & METHODS: In order to provide comparative data for this project, two design concepts were created, using several componential programmes of Ansys, including DesignModeler, Ansys Meshing, and Fluent. The first was a typical, conventional solar thermal flat plate collector, with five rigidly and linearly arranged copper thermosyphon pipes running through its interior. The second was an original biomimetic flat plate collector. Although similar to the first, conventional flat plate collector design with regard to the composition of its glass cover, aluminium absorber plate, and polyurethane insulation, the composition of the copper thermosyphon network of the biomimetic flat plate collector differed significantly, taking the vascular arrangement of the Sweetbay Magnolia (*M. virginiana*) leaf as the source of its inspiration. The selection of a leaf as the source of inspiration for the design came down to the similarities drawn between leaves and flat plate collectors in terms of their absorption and conversion of solar energy, as well as the mechanisms by which they transport water throughout their systems. Once conceived, these models were developed upon, in order to assess how the variances in their operational behaviours may change when additional or substitutional components were added/included within the designs. This was done by, firstly, by incorporating PV panels atop the flat plate collectors to then form photovoltaic thermal (PVT) systems, one conventionally shaped and one leaf-shaped. The second additional system type that was tested included the substitution of the phase change material (PCM) palmitic acid, in place of the existing polyurethane insulation, to form a hybrid PV/PCM system, again with one conventional and one biomimetic design. This meant that a total of six models were developed and tested within Ansys over the duration of the project. Simulations were run on the various models within Ansys Fluent. Through the use of Fluent's "solar calculator" function, it was possible to test all 6 of the models under ambient conditions, namely solar irradiance, which were accurate to the location at which the simulations were being run; the Civil Engineering laboratory of Trinity College Dublin. The benefit of applying such a technique is that the data produced through these simulations can be used as comparative evidence should any physical experimentation ever be carried out using similar/identical designs. During simulations, particular emphasis was placed on the data concerning both thermodynamic output variables, such as solar heat flux, absorbed infrared solar flux, reflected infrared solar flux, and overall system temperature, as well as hydrodynamic output variables, including flow velocity, pressure, turbulent kinetic energy, and vorticity.

RESULTS: Due to the complexities of the models created, both in their construction and in the heavy demands placed on their components during simulations, the data regarding heat transfer throughout each of the system types proved to be largely unconstructive in determining whether the results favoured the conventional or biomimetic designs, with inconsistent heat distributions, extreme temperatures, as well as

poorly conductive components observed. It is likely that these errors may have arisen due to a lack of detail within the models, most-specifically within the meshes of the respective designs. This could be due to the fact that, for a considerable portion of the time allocated to the completion of this project, only Ansys Academic was available for use, as the laboratory facilities of Trinity College Dublin, which were equipped with full Ansys licenses, were closed due to the COVID-19 pandemic. This use of Ansys Academic meant that strict limits were placed on the number of elements and, thus, the degree of detail and structure, that could be applied to the models during the meshing process. Another potential source of error may have lain within the finer details of the boundary conditions, but such an error would be quickly identified and remediated should further testing on these models be carried out.

However, the hydrodynamic data produced by all six models appeared accurate, promising and favourable to the biomimetic systems upon analysis. The more rigid, conventional designs produced flow velocities of greater disparity, with extremes in both high and low values observed. As a result of the extreme high flow velocities, isolated regions of significant vorticity and turbulent kinetic energy were also witnessed throughout much of the copper thermosyphon pipes of these designs which, in practical use, could lead to lead to damage in the long-term due to abrasive action. The extreme low flow velocities resulted in numerous areas of almost complete stagnation within the thermosyphons of the conventional designs, which would result in an overall inefficient thermal system in practice. Contrarily, the biomimetic, leaf-shaped designs of the novel systems demonstrated significant improvements within the same output variables. Steady, more uniform flows were observed throughout the entirety of the biomimetic thermosyphon networks which, in turn, lead to far lower values and far fewer incidents of turbulent kinetic energy, as well as no areas of significant stagnation.

CONCLUSIONS: The results produced by the simulations performed in this study demonstrate genuine promise in the application of leaf patterns to the design of solar energy systems, with the hydrodynamic performance clearly benefiting from the Magnolia-mimicking thermosyphon structure. Based on this finding, it is more than plausible that biomimicry in general has the potential to bring about significant improvements in both the solar thermal and solar photovoltaic systems of the future. It is highly recommended that other, potentially applicable biomimetic design concepts be explored and tested in order to identify further ways in which current state-of-the-art designs can be improved.

OPTIMIZING CARNOT BATTERY CONFIGURATION FOR WASTE HEAT RECOVERY INTEGRATED SYSTEM WITH ORC

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INTRODUCTION: Utilization of waste heat and its conversion to power is in many industries not feasible due to high technological cost and the lack of incentives as renewables have. Some industries, however, often pay relatively high costs for the capacity reserve due to oscillations in electricity consumption influenced by the nature of the industrial process itself. These industries are also often abundant in the excess of waste heat which cannot be further utilized for heating or pre-heating purposes. Using this heat for power production by the means of thermally integrated Carnot Batteries then brings a very interesting opportunity for such industries.

MATERIALS AND METHODS:

This work presents an analysis of several configurations with focus on several aspects such as:

- Possibility of utilization of the upgraded heat in the industry
- Maximization of the waste heat utilization
- Applicability for pilot system

The novel configurations improving WH utilization and higher overall performance, while the upgraded heat (or generated cold) is at temperatures usable for the industry itself, are proposed, modelled, investigated and compared to the state of the art thermal cycles for Carnot battery systems. The main improvement point for the novel hot storage system is that during the discharging process, heat for the ORC is supplied both from the waste heat and the storage. Both the hot and cold storage concepts then are able to operate at reduced power also when the heat source is available and the heat from the storage is spent. On the other hand simpler configurations are also considered and performance is shown. These are mainly planned for a pilot application. Update and technical parameters on the progress of this planned pilot application will be reported in the last part of the contribution.

RESULTS: In the presentation. Introduction of a novel CB configuration. Comparison with state of the art thermally integrated pumped thermal energy storage based on ORC. Discussion of the improvements compared to the standard cycle. Finally design considerations for a pilot planned are presented and the technical parameters are shown.

CONCLUSION: In the conclusion, the novel CB system is proposed for further experimental investigation and to verify the increase in utilization and cycle efficiency compared to the simple CB configuration to investigate whether the increased complexity and cost of the overall system will be justified by an increase in WH utilization efficiency.

BUILDING STOCK QUANTIFICATION APPROACH FOR BUILDING RETROFIT ANALYSIS. A CASE STUDY FOR PV POTENTIAL AND ENERGY DEMAND REDUCTION

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INTRODUCTION: The European Union policies are encouraging the implementation of renewable energies as an alternative to fossil fuels dependency. This change has become a necessity due to the global warming effects, such as the rising temperatures, especially in the cities. According to those changes, analyzing the large-scale potential around the territories and the cities' potentials can provide insights to the policymakers. The following methodology enables us to estimate the roof availability for electricity generation and the energy demand. Thus, provides the opportunity to evaluate, at the same time, the self-consumption possibilities and the retrofit requirements of the stock for the different municipalities.

MATERIALS AND METHODS: The methodology consists of the quantification and characterization of the residential building stock according to three key parameters, the year of construction, the building typology and the number of floors. According to buildings' characteristics, the energy demand and the roof potential can be quantified and compared among the different municipalities. Catalonia has chosen as a case study of this methodology to verify the "Energy Transition" possibilities. The selected region consists of 922 municipalities, which includes Barcelona as a big city.

RESULTS AND CONCLUSIONS: Results have shown that for the selected case study, the residential demand of the cities is covered between 8 and 25%, depending on the size and the characteristics of each city. It has also shown that more than 63% of the buildings were built before the 70's, with no insulation and important energy demand for building conditioning, requiring important building retrofit. The model has shown the necessity to reduce the energy demand of those buildings by 80%, which can be improved by a wide range of technologies, such as insulation, double-glazed windows, appliances renovation or district heating, among others.

DEMAND ORIENTATED STEAM GENERATION FROM PHASE CHANGE MATERIAL BY USING A ROTATING DRUM HEAT EXCHANGER

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INTRODUCTION: During the discharge process of a latent heat storage, phase change material solidifies at the heat transfer surface, which decreases the heat transfer. In the presented rotating drum heat exchanger for latent heat storage a rotating drum is partially immersed in liquid phase change material. While water evaporates as it passes through the drum, the liquid phase change material solidifies at the outer surface of the drum. The solidified layer is removed by a fixed scraper at each rotation and the solid phase change material is stored in a separate tank. This leads to a high surface specific heat transfer and a separation of power and capacity. In the presentation, a complete heat storage system based on a rotating drum heat exchanger and sodium nitrate as phase change material for the demand-oriented generation of steam for industrial processes as well as for electrical power generation is discussed based on theoretical and experimental research conducted with a laboratory pilot of the rotating drum heat exchanger.

METHODS: Three different designs of the drum are discussed: a drum completely filled with water, a drum with concentric annular gap and a drum with several individual tubes drilled into the drum wall. The concepts are examined analytically and numerically with respect to heat transfer capacity, maximum operating parameters and technical feasibility.

RESULTS: While a drum completely filled with water is predestined for the generation of low-pressure saturated steam for industrial processes, superheated steam can be reached with a concentric gap. High-pressure steam can be generated by using several individual tubes within the drum wall. The achievable heat transfer during the discharging process is exceeding 0.5 MW per meter of drum length at a drum diameter of 1 m. The storage system can be charged directly either by electric heaters or by using suitable heat pumps.

CONCLUSION: With the rotating drum heat exchanger for latent heat storage, steam can be generated with constant power and high heat flux densities of above 200 kW/m² based on the drums outer surface. The design can be realized on an industrial scale in the MW range.

EXPERIMENTAL STUDY ON THE EFFECT OF FLAT AND THIN SLAB ENCAPSULATION DESIGN ON A PCM TANK

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INTRODUCTION: Thermal energy storage (TES) is proved to be one of the most effective solutions to enhance the penetration of suitable energy resources and increase the performance of energy systems. Latent heat thermal energy storage (LTES) attracted the attention of researchers in the last twenty years due to the possibility to exploit the phase change of storage materials ensuring a high energy density in a nearly isothermal operation. The design of the encapsulation of the PCM is critical to define both amount of energy stored and the thermal power to be delivered from and to the system. This paper analyses experimentally the performance of the PCM tank with two different designs of flat slab provided by PCM products within the EU-funded SWS-Heating project.

MATERIALS AND METHODS: The lab-scale PCM tank was designed to contain around 40 kg of the PCM encapsulated in two different containers with rectangular shapes with a volume of 3 liters (FlatICE) and 1.7 liters (ThinICE). Therefore the total amount of PCM that fits in the tank was of 60.5 kg and 42.5 kg for FlatICE and ThinICE, respectively. The experiments were performed connecting the storage tank to a closed single water loop used to charge and discharge the PCM. The heating power was supplied to the loop using 3 electric heaters with a total power of 5 kW. On the other hand, cooling power was provided by a 7 kW air/water condensing unit. Tests were performed to evaluate the effect of the type of slab on the inlet/outlet temperature distribution, discharge power, and energy stored.

RESULTS: The different design of the slabs and the different amount of PCM, allowed the FlatICE slabs to store 20% more energy compared to the ThinICE. However, the ThinICE showed better results in terms of specific energy density storing 0.075 kWh/kg compared to 0.06 kWh/kg obtained with the FlatICE. However, the results showed that in the charging process the outlet temperature profile is similar in both types of slabs. In the discharging process, although the two encapsulation showed a similar initial peak in the power delivered (around 3 kW), the FlatICE was able to maintain a higher power for a longer period of operation compared to the ThinICE and therefore the higher outlet temperature.

CONCLUSIONS: In this study, two types of PCM slabs were analyzed and compared experimentally. For the desired application the FlatICE slab showed better allowing to store more energy in the same tank. Both types of encapsulation showed a similar peak power. Results show that even the FlatICE managed to maintain the outlet temperature of the storage tank for periods of time 2.5 times longer, the ThinICE showed better performance in terms of specific energy density.

ANALYSIS OF THE BEHAVIOR OF A THERMOCLINE TANK CONSISTS ON A PACKED BED WITH SOLID PARTICLES

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It is indisputable that the energy model is changing towards to a sustainable model that involves the use of renewable energies. The main drawback of renewables is their intermittent nature and the existing mismatches between production and demand. The solution to satisfy consumption needs during non-production periods is through thermal energy storage.

Packed beds are simple and economical systems for thermal energy storage purposes. For years, they have been widely used for sensible thermal energy storage due to simplicity and low cost. Sensible energy storage with packed bed systems has been a successful solution for a variety of low-medium temperature applications such as in greenhouses, in buildings for providing a solar contribution of the domestic hot water or a space heating demands. The main advantage of packed beds is their characteristic temperature stratification providing a considerable temperature gradient.

This work presents the thermal behavior of a dual-thermocline tank in solar energy applications at low-medium temperature ($T_{in} = 300^{\circ}\text{C}$). The simulated tank is based on a laboratory-scale experimental facility and has dimensions of 0.58m in diameter and 1.8m in height. Inside the tank, two phases can be distinguished: 60% solid phase (solid particles) and the gas phase, that is the Heat Transfer Fluid (HTF). The computational domain consists of an axisymmetric tank of cylindrical shape filled with different types of sensible heat materials. The thermodynamic properties of both phases are temperature-dependent. The tank is insulated by means of 100 mm thick mineral wool layer.

In this study, charging and discharging phases are independently analysed. Charging phase consists of introducing hot air through the upper part of the bed and the discharge phase is conducted by the lower part of the bed. Computational Fluid Dynamics (CFD) simulations were carried out with COMSOL Multiphysics®. The governing equations were solved for incompressible turbulent flow based on two-phase transient model Equation to calculate the temperature of solid and fluid phases. The proposed model for this 2D axisymmetric transient model shows a good agreement with the experimental results of the reproduced facility with a computational cost that is moderate. The model developed will be extensively used for sensitivity analyses, proving the potential of thermocline storage for cheap and efficient application in power plants and grid management.

LOW-EMISSION HEAT SUPPLY WITH HEAT PUMPS AND HOT WATER STORAGE – OPTIMAL DESIGN AND OPERATION

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INTRODUCTION: A new concept for the energetic development of a zero-emission quarter (living lab) is currently being investigated within the framework of the joint project „Demonstration of German Energy Transition in Zwickau“. This project started as part of the funding initiative of the German Federal Ministry of Education and Research and the German Federal Ministry for Economic Affairs and Energy „Solar Building/Energy-Efficient City“ and was launched in November 2017. The emission-free heat supply, the security of supply and socially acceptable heating costs are important criteria. The present system design provides the use of heat pumps and thermal energy storage.

MATERIALS AND METHODS: The current work deals with the use of return flow of an existing district heating network as the heat source of the heat pumps for the quarter heat supply. In the present case, the district heating network is operated with a biomass cogeneration plant. The power supply of the energy central (quarter level) is based on renewable energies. Only a limited district heating return volume flow is available for the energy center. An optimal design is necessary to fulfill the above-mentioned goals while adhering to the constraints. TRNSYS 18 is used for modeling and simulation of the heat supply system. The electrical load caused by heat pump operation can be regulated and contribute to the stabilization of the electricity grids. Here, the thermal energy storage plays a key role in this process. Depending on the dimensioning of the system, an advanced production of heat is possible when conditions are particularly optimal (low electricity costs or surpluses from renewable energies). The CPLEX Optimizer is used to investigate the optimization of operation and system flexibility in terms of heat generation and supply.

RESULTS: The parameter studies demonstrate the effect of different influencing factors such as the heat capacity of heat pumps, storage volume and energy costs, which are important for the fulfilment of the project goals. Operational optimization by means of mixed integer optimization shows that a high flexibility potential is created by the use of the thermal energy storage.

CONCLUSION: Compared to the reference system without the thermal energy storage, almost 60% more heat could be produced under favorable conditions.

USE OF REINFORCEMENT LEARNING TO OPTIMIZE THE CONTROL OF SOLAR THERMAL COLLECTORS COUPLED TO SEASONAL THERMAL ENERGY STORAGE

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INTRODUCTION: An optimum control is one of the most promising ways to increase the efficiency of systems formed by solar fields coupled to thermal energy storage (TES). The discontinuity of solar irradiance, thermal demand, and the complexity of the system itself make a very challenging task to reach an optimum control. Traditional rule-based control (RBC) strategies are not able to foresee the optimal control decisions of a system with such characteristics. Reinforcement learning (RL) control, which is a smart control technique, has presented lately very good results to find the optimum control of energy systems. In the present study, optimal control based on RL of a complex seasonal system formed by solar thermal collectors and three types of TES systems that supplied heat to a building was studied within the EU-funded SWS-Heating project.

MATERIALS AND METHODS: The system under study, located in Nuremberg (Germany), had the following subsystems: evacuated tube collectors, a phase change material (PCM) tank, a sorption tank, a water tank, and a back-up boiler. The system stored solar heat in summer in the sorption tank and released it in winter for space heating (SH), assisted by the PCM tank. Moreover, throughout the year solar heat was also short-term stored in a water tank for SH and domestic hot water (DHW) applications. A boiler was used when solar heat couldn't provide the required heat demand. Every subsystem was modelled in Python either following analytical equations (evacuated tube collectors, boiler), finite volume method (PCM tank and water tank) or a performance map based on experimental data (sorption tank). The connection between subsystems was done in an implicit approach (except the water tank) based on Gauss-Seidel method. A smart control based on RL techniques and also developed in Python was used to optimize the control of the system. RL technique is a smart control method where the controller learns the optimum action based on a reward, in this case, the operational costs of the system. A RBC strategy was used as reference to analyze the performance of the smart control.

RESULTS: The results show the suitable action to be taken by every subsystem at every time-step to reach the minimum operational costs. These decisions are based on the system inputs (ambient temperature, solar irradiance, thermal demand) and the states of the system (state of charge of the different TES). The smart control based on RL techniques operates the system reducing the operational cost around 9% in comparison with the RBC. Nevertheless, during winter, the seasonal system must be assisted most of the time by the back-up boiler.

CONCLUSIONS: In this study, a RL control technique was implemented into an innovative complex seasonal system to supply DHW and SH for residential applications and results were compared against a RBC. Despite the better results obtained by the smart control (9 % cheaper), during winter the back-up boiler had still to assist the seasonal system. In the extended paper, detailed information about the control actions taken by every subsystem will be presented.

EFFECTIVE THERMAL CONDUCTIVITY FROM THERMAL RESPONSE TESTS INCREASES WITH TIME WHEN SUFFICIENT GROUNDWATER FLOW IS PRESENT

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INTRODUCTION: Thermal response tests (TRT) are used for dimensioning of borehole heat exchangers and borehole thermal energy storages (BTES) (Gehlin and Nordell, 1997, Signorelli et al. 2007, Liebel et al. 2011). The test is based on the assumptions that conduction is the primary heat transfer mechanism, and that all other heat transfer effects can be accounted for by using an effective thermal conductivity rather than the thermal conductivity of the ground (Liebel et al., 2011). This effective thermal conductivity is found from the TRT results. Several studies on TRTs in boreholes with groundwater flow, report that the achieved thermal conductivity increases with test time (Witte, 2007, Holmberg et al., 2018). This increase is a challenge for correct dimensioning of the BTES because it makes it hard to determine which value of the effective thermal conductivity that should be used in design. Poor dimensioning will result in either insufficient capacity of the BTES or higher installation costs than necessary. Thus, the groundwater's effects on heat flow enhance uncertainty of both sizing and costs of BTES. There are also some cases where the effective thermal conductivity is hard to determine, or the established method does not apply (Sanner et al., 2000). As convection is proportional to temperature and conduction to the spatial temperature derivative, the effective thermal conductivity cannot completely account for convection. Signorelli et al. (2007) proposed to apply a full numerical simulation for design if convection effects are present. The drawback of numerical simulation is that it requires modelling skills, advanced and often expensive software and much time. This work proposes a simple solution to the problem with TRTs that show increasing thermal conductivity, without advanced numerical simulation or expensive software.

MATERIALS AND METHODS: Mathematical deduction is used to find an explanation for the increasing value of the effective thermal conductivity in boreholes affected by groundwater flow. Thereafter, a physical interpretation of the explanation is provided, and an alternative form of the line source equation is developed to account for the groundwater effects. TRT-data from groundwater filled and open boreholes in crystalline bedrock in Norway with high groundwater flow are used to find the thermal conductivity as a function of time by the established standard method. The result is plotted together with the theoretical line predicted by the mathematical deduction using the same borehole equivalent resistance to evaluate the explanation. Thereafter, both the established standard equation and the alternative equation proposed here are applied to the measurement data. The two parameters of the equations are found by linear regression and parameter fitting, respectively. The predicted temperatures from these parameters and equations are plotted and compared to both each other and the measurements.

RESULTS: A simple explanation is found mathematically, and predicts that in a pure conductive field, the effective thermal conductivity will increase infinitely, proportionally to the logarithm of time. A reasonable physical interpretation of this is that the temperature increase when injecting heat should be proportional to the logarithm of time when pure conduction can be assumed. However, when this assumption is not valid, and heat is carried away by groundwater flow in addition to conduction, the temperature will approach a steady-state temperature. This is achieved in one of the presented TRT-results. However, the line source equation still predicts a change proportional to the logarithm of time, and moves this dynamic

ENERSTOCK 2021

Short oral lectures/posters

change to the only other variable in the equation: the effective thermal conductivity. This explanation seems reasonable from the achieved effective thermal conductivities in this study, but no final conclusion can be drawn without more data. The achieved effective thermal conductivities become significantly higher (up to 64 W/(mK)) than the expected values of rock based on mineralogical composition and porosity.

An alternative form of the line source equation which takes the convective effects of regional groundwater flow into account is developed. The TRT results are well imitated by both the standard and the proposed method, yet, the proposed method reduces the sum of squared deviations by 44-77%, and is more physically correct. Hence, when the effective thermal conductivity becomes significantly higher than the thermal conductivity of the rock, is hard to determine and/or the standard method is inapplicable, the method proposed here could be applied instead of the line source equation. The thermal conductivity of the rock accounts for conduction while a convection coefficient accounts for the convection. The convection coefficient and the borehole thermal resistance are found by parameter fitting. A simple schematic for when and how to use the proposed method is presented.

CONCLUSION : When significantly high groundwater flow affects a borehole, the existing method by applying the infinite line source equation gives unrealistic results. The achieved effective thermal conductivity increases with time, because the temperature approaches a steady-state temperature where heat input and heat removed is balanced. In these cases, convection cannot be neglected . The proposed equation takes both conduction and convection from regional groundwater flow into account and can be applied for analysing the TRT data instead of using the established solution to the infinite line source. The proposed equation is applicable also when the established equation cannot be applied, is more physically correct and requires no modelling skills, expensive numerical software or similar.

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OPPORTUNITIES FOR BTES IN EXISTING BUILDINGS – IDEAS AND FIRST RESULTS FROM PROJECT GEO4CIVHIC

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INTRODUCTION: A major obstacle to decarbonisation in the building sector is the comparably low share of new construction, and the specific problems encountered when supplying heat and/or cold from renewable energies (RES) to existing, and in particular older, buildings. Without a solution to the problem of RES in refurbishment, however, the decarbonisation of the building stock will simply take too long. Shallow geothermal technologies like UTES have contributed substantially to decarbonisation in new construction. However, for a wider deployment in existing buildings, in particular in historical ones, the technologies need to be developed further and innovative ideas must be tested and brought to the market.

MATERIALS AND METHODS: Within the EU-funded project GEO4CIVHIC a survey was done to identify and understand all other possible barriers to BTES in existing building environment, be they technical or socio-economic, and the project partners work on suggestions for suitable solutions. The work then addressed two principal barriers, which are construction of ground heat exchangers under constrained site conditions, and adaption of heat pumps and other components to older heating/cooling systems. A specific emphasis is given to historic buildings, i.e. those dating from before the mid of the 20th century, including listed buildings, where the constraints are more severe. Development work is done to provide technical solutions for overcoming these barriers, e.g. with novel drilling tools and enhanced heat pumps. Several demonstration cases are under development to test the solutions found (4 real sites in Belgium, Ireland, Italy and Malta, and 12 “virtual” sites, where theoretical case studies for renovation with borehole heat exchangers are performed on real, existing buildings).

RESULTS: Less invasive, less costly and quicker drilling and installation methods for borehole heat exchangers (BHE) have been developed, partly drawing on results from the previous H2020-project Cheap-GSHPs and others. Also material development within the parallel project GEOCOND is taken into account and respective novel BHE materials are included in the tests. Test installation is partly performed on some pilot sites, and will continue at the 4 real demonstration sites. The size of the examples, in particular the “virtual” case studies, varies widely and comprises small systems with a few BHE as well as larger, true BTES installations.

In addition to new hardware, a Decision Support System is under development to help owners of potential renovation project in assessing if a geothermal system can be installed on a certain site and for a certain building, and if so, which options might be the most economically interesting ones. A database and GIS-system for suggested drilling method and estimated drilling cost is already implemented.

The presentation will give an overview of the project and explain the barriers identified, and will then focus on the new development to overcome barriers for drilling and BHE installation in the built environment, in particular for BTES applications.

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ENERSTOCK 2021

Short oral lectures/posters

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MODELING OF THE TOTAL EFFICIENCY OF HYBRID PHOTOVOLTAIC/THERMAL COLLECTOR WORKING IN THE DIRECT SOLAR ENERGY ABSORPTION MODE

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Solar irradiation can be harvested in a form of thermal or electrical energy using respectively solar (T) collectors and photovoltaic (PV) cells. Depending on the construction and type, the efficiency of T collectors is on the order of 50-70% and for PV cells 10-20%. The first studies have shown, that hybridization of T collectors and PV cells may significantly increase the total efficiency of the system [1]. Thereafter, non-transparent or semi-transparent working fluids containing dispersed particles were proposed for direct solar absorption that has its benefits compared to conventional T collectors. Finally, in order to maximize the efficiency, solar spectrum splitting technology was proposed to harvest thermal and electrical energy at the same device [2].

This study focuses on the evaluation of the total efficiency of a hybrid photovoltaic-thermal collector (PV/T) that utilizes direct absorption to make clear what is the electrical, thermal and total efficiency that are expected. The following effects occur in PV/T collector: i) direct absorption of the part of the solar radiation spectrum by the liquid and its conversion into the heat, ii) absorption of the remained part of the solar radiation spectrum by the PV cells and its conversion into the heat and electricity, iii) heat exchange between PV cells and the liquid flow, iv) heat losses to the ambient in the form of radiation and convection.

The solutions of fullerene C60 (CAS #99685-96-8) in tetralin (CAS #119-64-2) with the mass fraction up to 0.0010 kg·kg⁻¹ were considered as working fluid. Unlike numerous others, the solutions of C60 in tetralin have excellent colloidal stability [3]. It is well known that the peaks of spectral response of crystalline silicon solar cells are between 850 and 950 nm, and their precise shape is influenced by cell process details especially the antireflection coating [4]. At the same time, the solutions considered in our study of C60 in tetralin have a high absorbance value at very low mass fraction of C60 in the range of 350...650 nm with the spikes located between 340 and 420 nm.

The experimental data on thermal conductivity, viscosity, density, specific heat capacity, and light absorbance of these solutions has been obtained experimentally [3]. The absorbance spectrum of tetralin/C60 solutions was considered during the modeling of a PV/T collector.

A crystalline type of silicon solar cell was chosen as a component of the hybrid PV/T collector because they are the most affordable and commonly used. It is well known that the efficiency of the PV cell significantly decreases when the temperatures of cells rise. Accordingly, PV/T collector has one more benefit i.e. PV cells cooling that allow to keep its efficiency at high level. Thereafter, the temperature dependence of PV cell efficiency was taken into account in the simulation.

The CFD modeling of the hybrid PV/T collector has been performed as follow: the solar radiation intensity, the ambient temperature and heat transfer coefficient from PV/T collector to ambient air were fixed during the simulation; the mass fraction of fullerene C60 in tetralin and the thickness of the liquid layer and, as a

ENERSTOCK 2021

Short oral lectures/posters

consequence, the flow rate were varied during the simulation; a negligibly small heat transfer from the PV/T collector cross-cut ends was assumed in the simulation.

The prospects of hybrid PV/T collectors with direct solar absorption have been justified as a result of the study. Moreover, the absorbance spectrum of tetralin/C60 solutions is not optimal and the overall efficiency of PV/T collector can be improved by using other liquids/particles combinations.

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DESIGN AND BUILD OF A NOVEL DUAL-TUBE PCM STORAGE UNIT

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INTRODUCTION: To allow for a de-coupling of the charging and discharging parameters, a dual-tube PCM storage unit using extruded aluminium fins was designed and built. This concept allows on the one hand for completely different media and flow parameters to be used, it also allows for temporally independent charging and discharging, simplifying system integration and control. This is a benefit for industrial systems, in which differing systems can be coupled through a storage unit, allowing for serial or parallel charging and discharging, with differences in power or capacity balanced by the storage unit. A 160 kWh storage unit has been analysed, designed, built and will be experimentally tested by the conference.

MATERIALS AND METHODS: The extruded aluminium fins are used due to their design flexibility, high thermal conductivity and proven methods for assembling the fins to the tubes. The storage unit is designed for use with nitrate salts, in this case a eutectic of lithium nitrate and potassium nitrate with a melting temperature of 133 °C. The design of the fins and storage are conducted using a combination of an ANSYS® Fluent® analysis and a numerical Matlab® model. The designs are analysed and optimized for manufacturing constraints, cost as well as thermodynamic goals and limitations. Build considerations and overall capacity are determined from the heat source and sink in the system.

RESULTS: The design method developed shows great design flexibility for varying charging and discharging parameters. This range is detailed in a parametric study. The dual-tube fin has been successfully produced and the storage unit built.

CONCLUSIONS: The novel dual-tube fin that will be discussed and presented is coupled between a heat pump system and an ORC system, using differing refrigerants as well as flow parameters for charging and discharging. The design process shows the flexibility, options and complications in designing a storage unit that matches both charging and discharging parameters. The transfer from the design of the fin to the design and build of the storage unit shows the tremendous potential of this novel design, with headers and tubing optimized for the charging and discharging parameters and media. The operation of the storage unit will give insight into the actual heat transfer across the fins, specifics regarding commissioning of this storage design as opposed to a mono-tube storage unit, as well as operation of separate charging and discharging systems. The presentation discusses these various aspects design method, build of the storage and analysis of this novel latent heat thermal energy storage.

LIFE CYCLE ASSESSMENT OF AN INNOVATIVE HYBRID ENERGY STORAGE SYSTEM FOR RESIDENTIAL BUILDINGS

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INTRODUCTION: The buildings sector is one of the less sustainable activities in the world, accounting for around 40% of the total energy demand. The use of energy storage systems can contribute to the buildings decarbonization by achieving a reduction of building electrical consumption needed to keep the comfort conditions and. In Mediterranean climate regions, buildings are usually equipped with air-conditioning systems since cooling requirements can be critical in summer periods, while in continental climate regions, heating demand is elevated. Therefore, this study presents the environmental impact through a life cycle assessment (LCA) of the electrical and thermal storage system in both Mediterranean and continental climate zones, compared with a conventional reference system within the EU-funded HYBUILD project. This approach is the path to get the best eco-efficient solution, identifying possible improvement decreasing environmental impact across all life cycle stages.

MATERIALS AND METHODS: This study is based on the methodologies ISO 14040 and 14044 for obtaining quantitative results on the environmental impact, from cradle to grave. Thus, this LCA is based on the impact assessment method ReCiPe in impact points and GWP in kgCO₂eq. The database used was Ecoivent 3.6. Moreover, this work encompassed three distinct phases of evaluation: manufacturing, operational, and end of life. The goal and scope of this analysis were focused on the system and not on the whole building and the objective was also to evaluate the environmental impact of the innovative subsystems. The functional unit used is 1 kWh of consumed energy and 30 years of the lifetime for these systems is considered.

RESULTS: Preliminary results show the environmental impact of the system in different climate zones, and also the impact of the different components in the system studied. As expected, the innovative hybrid system presents, in its manufacturing stage, a higher impact than the reference system due to its greater complexity. However, due to the low energy consumption during the operational stage, the hybrid system showed the best environmental performance than the reference system.

CONCLUSIONS: In spite of the environmental profile of some components of the system in the manufacturing stage is higher than anticipated, the environmental efficiency of the studied system showed a good behaviour in the operational phase of its entire life cycle.

LARGE-SCALE COLD WATER STORAGE - GERMAN STATE OF THE ART

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In Germany, large-scale cold-water storage systems (500...7500 m³) were widely recognized over the last twelve years. Twelve large-scale storage systems were put into operation between 2007 and 2019. Correct storage function and suitable storage incorporation into the planned systems are two important preconditions in order to achieve the energetic, ecological and economic objectives. In practice, the advantages given here can be well exploited in operation (e.g. an improvement in energy efficiency and profitability). Storage hardware can be combined with compression and/or absorption chiller units. Storage units also enable a better use of air as the natural cooling source. This equipment is also widely acceptable for large to medium-sized supply systems for cooling in comparison with a retrofit of compression chiller units or ice storage systems. Flat-bottom tanks (volume greater than 500 m³) are in use in small-scale district and district cooling systems. The pilot storage unit's composition in segments could be used again in many follow-up projects (70 %). Specific storage units integrated into the building (500...1500 m³) close the gap in the field of the supply system for cooling of individual buildings.

In coming years, the energy efficiency and legal frame conditions will probably change. The abovementioned advantages are expected to become more important (e.g. ecological supply of cooling). Cold water storage systems like these can significantly contribute to making the entire energy supply more flexible. If, in the next few years, the production of renewable electricity (wind power engines, photovoltaics) grows, then the following trends may be expected: Use of renewable current for cooling with compression chiller units, Provision of negative secondary operating reserve or compensation energy by means of compression chiller units, Simultaneous generation of cooling and heat by means of heat pumps.

If, due to national restructuring of the electric energy supply, heating and power stations (e.g. gas-driven Motor-Block heating and power stations) expand more and more or the portion of electricity generated by means of power-heat coupling increases, then power-heat-cooling coupling (e.g. very high utilization of the primary energy source) could still become more important again. Consequently, large-scale cold water storage systems provide significant advantages that are relatively independent of fundamental development trends.

NUMERICAL SIMULATION OF A FLUIDIZED BED WITH CONCENTRATED RADIATION DIRECTLY ON SiC PARTICLES

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Fluidized beds exhibit several advantages in the thermal energy distribution storage in concentrated solar power (CSP) applications thanks to their high mixing rates. For these favourable characteristics, fluidized beds with direct radiation on particles arise as a great promise for new generations of CSP plants. Many researchers have proposed the use of bubbling fluidized beds as a solar receiver/storage systems to avoid the typical corrosion problems and hot spots of these components, which often have to withstand temperatures above 1000°C during operation.

There are different simulation tools, which try to reproduce the complex behavior of a bubbling fluidized bed as closely as possible. Among them, Barracuda Virtual Reactor® is a unique Computational Particle Fluid Dynamics (CPFDF) software that was designed with the purpose to model particle-solid flows in fluidized bed systems. In contrast with other software, Barracuda presents a recently developed Eulerian-Lagrangian modelling technique based on a strong coupling between the fluid phase and particles named as multiphase particle-in-cell (MP-PIC). Thus, MP-PIC is an intermediate method based on Eulerian-Lagrangian model. MP-PIC is based on analysing the behavior of a group of particles (called "cell") of the bed, therefore, notably diminishing the required computational effort compared to a full Lagrangian model, which models the evolution of each individual particle within the bed. Contrary to Eulerian approaches, which also present a relatively low computational cost, as they model the fluidized bed as two fluids perfectly mixed, the 3D CPFDF simulation is able to provide detailed trajectories, distributions of solids, temperature in both phases, among others.

The results presented in this work were carried out using Barracuda V.R. v 17.4.1, being compared with experimental results obtained in previous works. Simulation models try to reproduce the same conditions given in the experimental tests. The bed has a height of 8 cm, with a diameter of 7.62 cm, containing silicon carbide (SiC) particles. In the simulation models, the bed walls are considered adiabatic and a total radiation flux of 30357 kW/m² was implemented at the top of the bed (directly on particles surface). This work performs a sensitivity analysis based on the simulation results of three different cases, each one corresponding to a different time step: 10^{-3} s, $5 \cdot 10^{-3}$ s, and 10^{-4} s, respectively. To ensure well-mixed bed, fluidization conditions of 2.5 times the minimum fluidization velocity, without radiation, have been introduced throughout the test, first leaving 240 s with fluidization only and 180 s more applying radiation. These initial simulations are the first step to validate the experimental results obtained previously. The sensitivity analysis shown in this work determines that the time step of 10^{-3} s is suitable, since the computational cost is lower and the maximum temperature difference with the other two cases is practically negligible (approximately 2°C). The computational time of each case with radiation has a computational cost of 7-8 days.

CFD ANALYSIS OF LARGE SCALE HIGH TEMPERATURE THERMAL ENERGY STORAGE UNIT

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INTRODUCTION: There is a growing trend to increase the renewable portion in the overall energy mix, this can be done by utilizing the full potential of renewable energy sources. In order to fully utilize the potential of renewable energy sources a storage unit is required which will store the excess energy produced and supply it when the demand is high, and production is low. The high temperature thermal energy storage (HT-TES) unit can provide the flexibility required, by storing the excess amount of energy in the form of heat and supplying it back either into the electric grid or any energy intense industrial processes.

MATERIALS AND METHODS: DTU Energy has constructed a vertical flow high temperature thermal energy storage (HT-TES) unit which uses air as a heat transfer fluid (HTF) and Swedish diabase rocks as a storage medium. This storage unit can store heat at a temperature of 675 °C and has a thermal capacity of 1 MWhth. In this presentation we aim to present our 3-D time dependent computational fluid dynamics (CFD) model of the rock-bed HT-TES developed in COMSOL Multi-physics 5.5. The model uses porous media and Local thermal non-equilibrium approach to solve this time dependent study. The model is first verified from the experimental data obtained from the pilot plant and then upscaled to 1 GWh to study the overall behavior of the system. The efficiency (for different charge rates), thermocline, and heat loss during the whole cycle (Charge-Rest-Discharge) period were studied.

RESULTS: The pilot plant model developed in COMSOL is satisfactorily validated from the experimental data obtained from the pilot plant at DTU. The charge efficiency of both the pilot plant and the upscaled version were ranging from 89-97% depending upon the time of charging and also the input power (charge rate). The pilot plant lost 21 % of total heat stored during the resting period of 72 hours while the upscaled version only lost 4 % during the same period.

CONCLUSION: An experimentally validated model is developed which can be upscaled according to the use case scenario to study the overall behavior of the system. The efficiency study for both pilot plant and the upscaled version showed that higher input power (charge rate) will provide higher initial efficiencies, however over a longer period of time the slower charge rate gives higher overall efficiency. The rate of heat loss is also much lower in the upscaled version. Thus, showing the benefits of upscaling the system.

“DIFFERENT CYCLE LAYOUTS FOR PUMPED THERMAL ENERGY STORAGE (PTES) SYSTEMS WITH ZEOTROPIC WORKING FLUIDS”

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Previously proposed Rankine cycle pumped thermal energy storage (PTES) systems utilize a pure working fluid at sub- or supercritical states. In the former case, phase-change materials are used to store the energy of the liquid-gas phase change of the working fluid, whereas in supercritical cycles, the thermal profile of a sensible hot storage network can be matched to that of the working fluid. In this paper a PTES system using a subcritical zeotropic mixture of ammonia and water is proposed. The ensuing temperature glide of the working fluid phase changes on the hot and cold storage side allow the use of existing sensible heat storage technologies. A theoretical framework for calculating the efficiency of the thermal cycle was developed, and simulations throughout a variety of parameters were performed. Relevant losses of the system are identified, and a corresponding loss-minimization approach is discussed. The resulting working fluid temperature in excess of 500°C allow the use of a combination of molten salt and pressurized water sensible thermal energy storage tanks. Furthermore, high-efficiency heat exchangers with low stream temperature differences need to be utilized. Using these currently available components from other industrial applications, such as concentrated solar power and district heating systems, a round-trip efficiency of 70-80% is attainable.

ENERSTOCK 2021

THURSDAY, 10 JUNE 2021

ORAL PRESENTATIONS

EXPERIMENTAL CHARACTERIZATION OF TWO LATENT HEAT STORAGE PROTOTYPES FOR DOMESTIC HEATING APPLICATION

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Latent heat thermal energy storage (LHTES) has a promising potential in various fields including power plant's waste heat recovery and residential building's heat management [1, 2]. By storing the excess energy during the production stage and utilizing it when needed, energy curtailment can be reduced and overall societal energy efficiency can be improved. Several different factors can influence the performance of a LHTES system, including the phase change material (PCM) properties, the heat exchanger in use, the amount of contained PCM, and the heat transfer fluid (HTF) inlet flowrate. Three major types of PCM applied in LHTES are: eutectic PCM, inorganic compounds PCM and organic compounds PCM. Among different organic compounds PCMs, paraffin wax is the most common product providing the advantage of high chemical stability and good energy density [3]. However, the low thermal conductivity of paraffin wax slows the heat transfer speed and prolongs the energy charging/discharging time. The common methods used to overcome the disadvantages of paraffin wax on macro scale are (1) encapsulation of PCM and (2) bulk PCM storage with extended heat exchanger (HX) surface [4]. For the first method, paraffin wax is encapsulated in specific casing configuration to increase the heat transfer area. The second method provides maintains the high energy density of LHTES with smaller HTF volume uptake. Both methods are experimentally investigated in this study.

Two designs of LHTES units have been tested for performance evaluation. The first unit is a 0.38 m³ tank containing slab-like macro-encapsulated PCM while the second unit is a 0.54 m³ tank containing spiral coil HX immersed in PCM. Charging/discharging tests were performed with temperature range of 46-72°C and parametric studies on HTF flowrate (0.15-1.5 m³/h for the slab macro encapsulation and 0.21-2.12 m³/h for the spiral coil HX) were carried out. Both constant and time-varying flowrate tests were performed. The maximum flowrate for the encapsulated case was chosen based on test completion time [1]; the maximum flowrate in the spiral coil HX unit was chosen proportional to the tank size. The supply HTF temperatures for both units were at 72°C and 46°C for charging and discharging, respectively. For the slab encapsulation unit, warm HTF was pumped into the tank from the top in charging, cold HTF entered from the bottom during discharging; as for spiral coil HX unit, HTF inlet was fixed at the top during both charging and discharging. During constant flowrate tests, the increase of the flowrate is inversely proportional to completion time in both charge and discharge. In addition, partial charge/discharge had higher mean power than the mean power of complete charge/discharge. In slab encapsulation, the smallest tested flowrate (0.15 m³/h) led to about four hours completion time, as the flowrate increase to 0.25 m³/h and 0.5 m³/h, the completion time decreased to 3 hours and 2 hours, respectively. The largest tested flowrate in the slab encapsulation unit (1.5 m³/h) took less than one hour to complete. In the spiral coil HX unit charging, HTF outlet temperature reaching 2°C below the supply HTF corresponds to a state of charge of 84% total capacity while only requiring 62% time of full charge. Similarly, with the spiral coil time-decreasing flowrate test mode in discharging, 54% of discharging time was achieved with 14% of capacity trade-off. Finally, the comparison between slab macro-encapsulated unit and spiral coil unit shows that the former shows higher thermal power while the latter has a higher energy storage density. At volume-specific equivalent HTF flow rate, charge and discharge for the macro-encapsulated unit took 1 hour to reach completion for an energy storage density of 31 kWh/m³, while charge/discharge for the spiral coil unit took 5 and 15 hours to reach completion at energy density of 58 kWh/m³.

In the spiral coil unit, a noticeable difference exists between the completion time of charge and discharge. For charging, the completion time with the smallest flowrate (0.21 m³/h) and the largest flowrate (2.12

ENERSTOCK 2021

Oral lectures

m³/h) was 20 hours and 5 hours, respectively. As for discharging, the completion time was 41 hours and 10 hours. This time difference is due to larger quantity of PCM in the spiral coil design where in charging, convection contributes largely to heat transfer mechanism. While in discharging, natural convection is negligible and the heat transfer may be solely done through conduction. Moreover, paraffin wax PCM has low thermal conductivity, which leads to the delay of discharging time.

This study shows that flowrate has a direct influence on LHTES system's charge/discharge completion time; partial charge/discharge effectively reduces the required time with a reasonable capacity lost. Lastly, while slab-encapsulation unit provides larger heat exchange area for HTF and PCM; spiral coil unit provides volume-efficient use of the storage tank, leading thus to a larger volume for PCM.

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ACTIVE PCM-BASED HEAT STORAGE USING BIOWAX AND A PILLOW-PLATE HEAT EXCHANGER IN A ZEB BUILDING

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INTRODUCTION: The Zero Emission Building (ZEB) lab (www.zeblab.no) in Trondheim (Norway), owned by SINTEF and NTNU, provides a structure to develop and test innovative solutions in a living laboratory. An innovative latent heat storage (LHS) unit using biowax as phase change material (PCM) has been integrated in the central water-based heating system. The LHS unit stores excess heat from the main heat pump and the district heating network. One challenge is to make use of the full potential of the PCM latent heat to have a compact and effective unit, while the unit itself should have a low associated CO₂-footprint.

MATERIALS AND METHODS: The integration of the LHS unit as an active component of the central heating system enables thermal buffering to support the heat pump. Depending on the heating demand in the building, the return temperature of the heating loop might be lower than 34 °C, and thus require additional power from the heat pump to sustain 40 °C as outlet temperature. Integrating the LHS unit downstream from the heat pump, with the option to circulate the return water through it or not, provides the opportunity to both charge and discharge the LHS unit, while smoothing the output demand from the heat pump. Charging the LHS unit occurs when the heating demand is low, using 40 °C as inlet temperature, as it is generated by the heat pump. Using a PCM with phase change temperature within 34-37 °C, return water at lower temperature than 34 °C can circulate through the charged LHS unit and be heated up before entering the heat pump. Additionally, the LHS unit can be directly charged using the district heating loop providing hot water at 47 °C. Another feature available with this integration is the opportunity to use the LHS unit as a direct heat source in the building heating loop. This is meant to occur when the LHS unit is charged and the heating demand in the building is relatively low. Therefore, the heat pump can be bypassed, reducing significantly the energy use during these low-demand periods. This operational mode is especially interesting if energy price is integrated in the control system of the overall heating system.

To be suitable to the application, the PCM should primarily have a melting temperature within 35-37 °C and limited supercooling. This limits the PCM selection to only a limited range of commercially available paraffin based PCMs. After investigation, the PCM CrodaTherm 37 (CT37) was selected due to its low degree of supercooling, its low-carbon footprint as well as its affordability. CT37 is a water-insoluble organic PCM, derived from plant-based feedstocks (Crodatherm, 2019). The PCM appears as a crystalline wax in solid state and oily liquid above melting temperature. In addition, CT37 has low flammability, which is an essential criterion in buildings. A sample of CT37 received by CrodaTherm was analysed by Thermogravimetric Analysis – Differential Scanning Calorimetry (TGA/DSC) at the SINTEF Energy Research Laboratory to evaluate the thermodynamic performance of the PCM. The average latent heat of fusion is 198.6 kJ/kg (+/- 0.9 %) and the average latent heat of crystallisation is 196.4 kJ/kg (+/- 0.7 %).

The heat exchanger containing the PCM includes 24 laser-welded stainless-steel pillow-plates, mounted vertically in parallel with a 40-mm pitch. Water circulates in each of them following a 2-pass pattern. Headers are gathered at one end of the unit to enable a homogeneous distribution of the water across the pillow-plates. The heat exchanger is filled with ca. 3 tons of PCM CT37 to occupy the volume between the pillow plates. A thick mineral wool thermal insulation around the LHS-unit allows for a theoretical heat loss under 1 % per 24 h.

RESULTS AND CONCLUSION: The aim of the project is to design and integrate a LHS unit in the central heating system of the ZEB Laboratory building in Trondheim (Norway). The LHS unit is designed based on

ENERSTOCK 2021

Oral lectures

pillow-plate heat exchanger filled with PCM whose phase change temperature is 35-37 °C. The designed LHS unit can store up to 194 kWh heat and simultaneously achieve sufficiently high heat transfer rates during discharge to successfully back up the heat pump for 2-3 days during the coldest winter days or be used as a heat source in the central heating system. Installation has been completed and the first tests are on-going.

THERMO-ECONOMIC ANALYSIS OF CASCADED LATENT-HEAT STORES IN PUMPED THERMAL ELECTRICITY STORAGE SYSTEMS

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INTRODUCTION: In pumped-thermal electricity storage (PTES) systems based on the Joule-Brayton cycle, sensible-heat packed beds are usually recommended as thermal stores. However, packed-bed stores, especially the hot store, require high-strength shells to withstand the high-operating pressures, which increases their cost. Cascaded latent-heat stores (CLHSs) are an option to replace packed-bed stores due to the non-pressurized vessels, higher energy densities and smaller sizes. In this work, the feasibility of a CLHS as the hot store in PTES systems is explored from a thermo-economic perspective. The effects of the total stage number (N) and NTU on the energy capital cost ($C1$), power capital cost ($C2$), exergy capital cost ($C3$), and exergy power capital cost ($C4$) are investigated.

MATERIALS AND METHODS: Multiple phase-change materials (PCMs) are arranged according to melting temperatures along the length of a tube-and-shell CLHS made of stainless steel. Argon, as a heat transfer fluid (HTF), flows through the PCMs at 10 bar while the store is charged. The HTF inlet and outlet temperatures are 773 K and 300 K, respectively, and the HTF flow rate is 12.5 kg/s. The charging time is 6 h. Thermodynamic optimization is performed based on the maximization of the total exergy storage rate. The analytical solution to the optimal melting temperatures is obtained and the maximum exergy stored is calculated.

The capital cost of the CLHS consists of the cost of tube-and-shell and of the PCMs. Three costing methods (Turton's, Seider's and Couper's) are used to estimate the capital cost of the tanks. The costs of adopted PCMs are assumed to be 5 USD/MJ of latent heat.

RESULTS: The effect of N on the thermo-economic performance is investigated. $C1$ and $C2$ both increase with N . When NTU is 0.8, $C1$ increases from 99 USD/kWh to 133 USD/kWh, and $C2$ rises from 592 USD/kW to 799 USD/kW as N increases from 35 to 50. For smaller NTUs, $C3$ and $C4$ also increase with N . When NTU is 0.8, $C3$ increases from 252 USD/kWh to 334 USD/kWh, and $C4$ rises from 1510 USD/kW to 2005 USD/kW as N increases from 35 to 50. However, for larger NTUs, the melting temperature in each stage tends to be higher than the environmental temperature for smaller N , which leads to minima in $C3$ and $C4$. When NTU is 5, minima of $C3$ and $C4$ exist for $N = 2$, which are 187 USD/kWh and 1121 USD/kW, respectively.

The effect of NTU on the thermo-economic performance is also considered, with all thermo-economic performance parameters increasing with NTU. When N is 20, $C1$, $C2$, $C3$ and $C4$ increase from 88 USD/kWh, 527 USD/kW, 227 USD/kWh and 1363 USD/kW, to 331 USD/kWh, 1988 USD/kW, 830 USD/kWh and 4981 USD/kW, respectively, as NTU increases from 1.2 to 5.

CONCLUSION: In this work, the effect of the total stage numbers and NTUs on the thermo-economic performance of a CLHS in PTES systems was investigated. Generally, CLHSs with low N and NTUs show good performance from a thermo-economic perspective, which needs further comparison with alternatives.

SIMULATIONS AND OPTIMIZATION OF BTES SYSTEMS FOR COMMERCIAL AND NON-RESIDENTIAL BUILDINGS IN PROJECT GEO: BASE, AND VALIDATION OF BHE SIMULATION

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INTRODUCTION: A national R&D-project funded by the German Ministry of Economics and Energy (BMWi) looks into optimized operation strategies for heating and cooling systems including borehole heat exchangers (BHE) (Kühl et al., 2019). In commercial and other non-residential applications these systems often are quite complex, with an array of different energy sources and supply units and numerous consuming points of heat and cold, and the size of the BHE field makes them a borehole thermal energy storage (BTES).

MATERIALS AND METHODS: Two industrial facilities, Leica Camera AG in Wetzlar, and a production hall at the Volkswagen AG works in Emden, are targeted in a campaign of scientific monitoring, documentation and evaluation of their energy supply and demand. Both sites contain a BTES system, with BHE in the case of Leica, and foundation piles as heat exchangers in the Volkswagen case. For comparison reasons, two more production facilities using a non-UTES thermal energy storage (TES) system as key component for heat and cold supply are considered in the project; these installations at Solvis GmbH and Oeding Print GmbH. Both in Braunschweig, also have a rather complex structure each. A fifth installation, the building of the E.ON Energy Research Center (E.ON-ERC) in Aachen, equipped with 41 BHE of 100 m depth each and monitored since several years (Stoffel et al., 2019), is used to calibrate the ground-side simulation and to test advanced control mechanisms.

RESULTS: While the setting up of the monitoring in the industrial BTES facilities is not yet completed (hampered by the restrictions to cope with the pandemic), an in-depth analysis of the different systems has been performed and preparations for simulation have been made, by representing the different components and their interaction. This presentation will focus on the BHE system at the E.ON-ERC and the simulation of the temperatures in the underground circuit based upon actual load data for heating and cooling. The BTES consists of three fields with one sub-manifold each, to be controlled individually; an advanced control system even allows to set and change the flow for each of the BHEs. Quick calculations with EED for the load data July 2018 to June 2019 resulted in a good match for most of the period. However, there were some deviations for intervals of continuous part-load operation in winter that need to be investigated further.

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METHODS FOR THE DETERMINATION OF THE STATE-OF-CHARGE OF A THERMAL ENERGY STORAGE DEVICE

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INTRODUCTION: Thermal energy storage (TES) is one of the most promising methods to make the implementation of renewable energy a viable and competitive solution to reduce the use of fossil fuels in various applications in buildings and industrial processes. The use of phase change materials (PCM) in TES systems is of special interest in solar thermal systems for heating and/or cooling applications in residential buildings. A correct and efficient integration of the TES system requires a proper components design and dimensioning, as well as the use of reliable monitoring and control strategies. However, to take full advantage of the TES system, the amount of energy stored in it, defined by a parameter called state-of-charge (SOC), is a key variable in the decision-making process. In this study, different methods were applied to estimate the SOC in a TES that implemented PCM for cold storage within the EU-funded HYBUILD project.

MATERIALS AND METHODS: A laboratory-scale prototype of an innovative three-fluid heat exchanger (3-fluid HEX) was used as a TES system and tested in an experimental setup available in the laboratory of the GREiA research group at the University of Lleida in Spain. An amount of 3.15 kg of commercial RT4 was filled into the 3-fluid HEX, which was used as evaporator of a simple compression refrigeration cycle, using R449A refrigerant, to cool a mixture of 30% glycol by 70% water used as coolant in the demand side loop. Three methods were applied to estimate the SOC of the TES, namely: temperature measurements at different locations in the PCM, estimation of the energy stored in the 3-fluid HEX, and air pressure measurements within the space where the PCM was placed. Energy balance in the refrigerant and coolant loops were used as a reference.

RESULTS: The results show the degree of accuracy of each of the methods studied, in terms of absolute deviations of the SOC values with respect to the reference values. In general, the method based on estimations of the total energy stored in the heat exchanger gave the best results, for which the maximum and average absolute deviations are generally less than 10% and 6%, respectively. However, the method based on the weighted average temperature of the PCM provided the best results for the discharge process, while for the charge process it still gave reasonable results. Applying the method based on pressure measurements, significant deviations of up to 50% were obtained with respect to the reference values.

CONCLUSIONS: In this study, three methods were applied to experimentally estimate the SOC in a 3-fluid HEX for cold storage. For the charging process, the method that gave the best results was the one based on estimations of the energy stored in both sensible and latent parts. For the discharging process, the method based on the weighted average PCM temperature seemed to give the most accurate results. Finally, the advantages and drawbacks of each method will be mentioned, as well as suggestions for possible future improvements.

ANALYSIS OF THE DISCHARGING PROCESS OF LATENT HEAT THERMAL ENERGY STORAGE UNITS BY MEANS OF NORMALIZED POWER PARAMETERS

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INTRODUCTION: Latent heat thermal energy storage (LHTES) enables a high storage density in narrow temperature ranges. However, one of the main disadvantage of most of the applied Phase Change Materials (PCM) is their low thermal conductivity. As a consequence, without optimization, LHTES generally have low charging and discharging powers. This is especially true for the solidification process. A variety of approaches have been developed to compensate for this shortcoming. So far, however, there is no method to fairly compare different concepts or designs. Therefore, within the working group PCM of the IEA SHCECES Task58-Annex 33 (<http://task58.iea-shc.org/>) on compact energy storage different performance parameters were reviewed, developed and tested. This paper summarizes some of the results achieved so far.

MATERIALS AND METHODS: A comparison of different LHTES concepts causes many difficulties, since among others the volume, the heat transfer fluid (HTF), the mass flow of the HTF as well as the initial and inlet temperatures of the HTF vary greatly between experimental setups. Based on an earlier publication, two performance parameters – one with slight improvements – are presented and applied for the first time to real experimental data. For this purpose, discharging (i.e. solidification) experiments from more than 10 different setups are used. In these experiments the above mentioned boundary conditions are varied within several of the setups. This allows a targeted verification of the suitability of the considered performance parameters, which are a normalized power and its mean value as well as a normalized UA value and its mean value.

RESULTS AND CONCLUSION: The mean values of the performance parameters are based on a weighting of the input parameters with the energy discharged. It is shown that a weighting with energy instead of time leads to a significantly greater comparability and also greatly reduces the dependence on the defined end of the discharging process. The normalization for the power is performed with the volume of the LTES – different definitions of this volume are discussed – as well as with a reference temperature difference. It was found that the interval from the initial temperature to the inlet temperature of the HTF is more

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convenient as reference temperature than the definition from an earlier publication. The normalization of the power significantly increased comparability, but the power and its mean are still highly dependent on the HTF and its mass flow. To overcome this limitation, a plot is introduced which shows the normalized mean power over the mean of a normalized capacity flow of the HTF. Plotting the experimental results in such a diagram reveals that the normalization worked well in most cases. In addition, the characteristics of the individual concepts and improvements introduced can be easily recognized. In the case of the UA values, the aim was to keep them independent of the HTF initially located in the LTES. However, the method envisaged for this purpose has proved to be useless. Therefore further approaches for UA will have to be developed and tested in the future.

EXPERIMENTAL STUDY OF AI-BASED MODEL PREDICTIVE CONTROL STRATEGY FOR THERMAL ENERGY STORAGE SYSTEM

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INTRODUCTION: Model predictive control (MPC) is an advanced control strategy that sequentially searches for optimal control points using a model that predicts the future behavior of a control subject and an optimization solver that searches for the optimum solution of control inputs. The MPC's performance depends on the accuracy of the prediction model and the efficiency of the optimization algorithm. In general, a building energy system has a non-linear behavior composed of various equipment. Thus, the modeling process is complicated, and the more accurate it is, the longer it takes to calculate. In the MPC framework, given the optimization problem must be solved in a real-time manner, computationally efficient and accurate prediction models are required. In this regard, MPC's practicality issue can be addressed using a machine learning prediction model and high-speed optimization solver. In this study, an MPC strategy was developed using AI techniques and applied to an experimental setup that mimics the building energy system with thermal energy storage (TES).

MATERIALS AND METHODS: The experimental system for cooling operation includes a chiller, thermal energy storage, heat exchangers, and variable-speed pumps. Air-conditioning space was replaced with a water tank and the cooling load was assigned by operating an electric immersion heater installed inside the water tank. Control variables are the flow rates of pumps in each water loop. As surrogate models, feed-forward type of artificial neural networks (ANNs) were used. Additionally, a metaheuristics optimization method was used to find optimal solutions with efficient constraint handling. A total of five ANNs were trained and constructed by using 3,103 data points collected from the experimental system. Hyperparameters of the ANN models were determined by trial and error approach and the best model was selected based on the evaluation against the separated datasets. The prediction variables using ANNs are as follows: Inlet and outlet temperatures of the chiller, temperatures inside the TES tank (top, middle, and bottom layer), the temperature of a water tank that is assumed as air-conditioning space, the power consumption of the chiller, and pumps. Constructed ANNs predict the future behavior of system parameters according to the flow rate variation and measured values at the previous timestep. The number of iterations on optimization calculations to find optimum control variables were set as 300 (10 populations and 30 generations). At each control timestep of 10 min, flow rates of pumps for the next 24-step were optimized to minimize the total operation cost. The accelerated experiment that shortens the day from 24 hours to 4 hours was conducted. To verify the effectiveness of the developed MPC strategy, a rule-based control (RBC) was also measured using the same experimental setup.

RESULTS: The developed MPC strategy was compared with the rule-based control (RBC) strategy. RBC strategy prioritizes the TES operation, and during the cooling operation, and when the TES tank is fully discharged, the chiller begins to operate solely to manage the cooling load. However, chiller efficiency depends on the energy consumed and the cooling delivered and it is affected by ambient temperature on part-load conditions. Therefore, in order to properly evaluate the results under different operating conditions, the correlation between the chiller's COP and part load ratio by the outdoor temperature was analyzed. Using the regression equation obtained through correlation analysis, the power consumption of

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the chiller was corrected to the value assumed to have consumed when the chiller was operated at the reference outdoor temperature. As a result, compared to the RBC strategy, the developed MPC strategy could reduce the operation cost by optimally manipulating a flow rate of supplying chilled water. MPC strategy could save the cost by 29% compared to RBC strategy, which began TES discharging simultaneously with the cooling operation, and by 18% compared to the case when TES started to discharge when the electricity price is highest. Also, constructed ANNs were evaluated by separated dataset and showed high prediction performance with R^2 larger than 0.9 and MSE less than 0.2 for the temperature prediction and MSE of approximately 0 in the prediction of power consumption. Therefore, predicted results from feed-forward ANNs in real-time operation were well agreed with the actual control output in time series. Moreover, the optimal control input could be obtained after completing 300 times of iterative optimization calculations averagely within 9 min.

CONCLUSION: In this study, the MPC strategy was developed using AI techniques and applied to an experimental setup that mimics a building energy system with TES. Experiments were conducted to verify the practicality of the developed AI-based MPC strategy. The MPC results were compared by two RBC strategies that prioritize TES operation and discharge the TES when the cooling operation starts and when the electricity price is highest. In conclusion, MPC could save operating costs 18–29% compared to RBC strategies. It is expected that the AI-based MPC strategy is sufficiently accurate and fast to realize real-time optimal control.

MULTIVALENT BATTERIES AND THEIR PERSPECTIVE

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Magnesium, calcium and aluminum are promising elements for future batteries due to the high gravimetric and volumetric capacities of metals. All three elements are highly abundant in the earth's crust with homogenous distribution on the globe. They are considered sustainable elements for batteries used in renewable energy storage.

Besides the above-mentioned benefits, there are several challenges connected with stripping and deposition of the metals, with the appropriate electrolyte formulation compatible with the metal anode and potential cathode materials, with current collectors, the housing of the cell and with the choice of appropriate cathode materials. Cathode materials allowing insertion of cations as we are using them in Li-ion batteries have limited applicability with multivalent cations. More appropriate are cathode materials that allow coordination redox reaction or conversion redox reaction. Among those, the highest applicability can be obtained with redox-active polymers and sulfur-based cathodes.

In this presentation, an overview of recent achievements in our group in the field of multivalent batteries will be discussed with a focus on the proper selection of battery components in order to achieve electrochemical properties attractive for commercialization.

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DEVELOPMENT OF AN H₂-PERMEABLE, PDCU-BASED, COMPOSITE MEMBRANE BY USING A REVERSE BUILD-UP METHOD

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INTRODUCTION: There has been increased demand for the production of hydrogen (H₂) for a low-carbon society. H₂-permeable membranes have been proposed to recovery pure H₂. Palladium copper (PdCu) alloy has been discussed for H₂-permeable membrane because of its long-term durability with relatively high H₂ permeability, selectivity. To obtain a large amount of high-purity H₂ for practical H₂ consumption processes, it is necessary to fabricate a membrane having a large surface area and allowing to form a stack for a large capacity of H₂ separation. Porous ceramic support for the Pd-based layer is generally used, but a ceramic material is vulnerable to thermal shock, and a flat plate figure has an upper limit of several cm order. A composite H₂ membrane with PdCu and metal support layer in plate figure by using a reverse build-up method has been investigated in this study [1]. The uniqueness of the proposed method is that the PdCu alloy layer was formed first and the metal support layer was later built on the alloy layer. The metal-supported PdCu composite membrane has durability on a thermal expansion and is able to extend the surface area and be stacked at multilayers. This study demonstrates the produced composite membrane by using the proposed method. Generally, in the fabrication of Pd-based H₂-permeable membranes, it is required to reduce the amount of Pd usage for cost reduction of the membrane due to the high cost of Pd. The thinning of a membrane is expected to reduce the diffusion resistance and significantly reduce the amount of Pd used [2]. The reverse build-up method for fabricating the composite membrane was originally developed to realize a membrane of a large surface area at a low-cost. By the method, it is possible to reduce the thickness of the PdCu alloy layer into several μm orders from 20 μm of conventional metallic rolling PdCu membrane. This study examined the production process and measure the hydrogen flux of the composite membrane. It was demonstrated that the required Pd amount of composite membrane is less than 1/8 of the conventional one for a unit amount H₂-permeable.

MATERIALS AND METHODS: The H₂-permeable, composite membrane, was fabricated using a reverse build-up method improved in this study. The reverse build-up method has four steps. At first, a polymer solution was coated on the glass plate for the formation of a resin primer layer. Subsequently, Pd₆₀Cu₄₀ (wt%) layer was deposited on the primer layer through a high-frequency magnetron sputtering. And then, electroplating was performed using a Nickel (Ni) plating additive to form a porous Ni support layer on the Pd₆₀Cu₄₀ layer. Finally, the glass plate was placed in a petri dish containing ethanol, wherein the resin of the primer layer was dissolved overnight to allow the removal of the composite membrane from the glass plate. Nickel layer in a previous process for Ni-plating layer forming was a dense and limited H₂ diffusion of the membrane. In this study, we improved the Ni layer porosity larger by introducing a new procedure and evaluated the H₂ permeation performance of the produced composite membrane.

RESULTS: Scanning electron microscopy (SEM) was performed to analyze a composite membrane prepared according to the reverse build-up method. It is evident from an SEM image of the cross-section that the

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prepared membrane has a two-layered structure comprising a Pd₆₀Cu₄₀ layer and porous Ni layer that acts as support, suggesting that the membrane is suitable for H₂ separation. The Pd₆₀Cu₄₀ layer and porous Ni layer were approximately 3.7- and 13- μ m-thick, respectively. The composition of the gas that permeated through the composite membrane was analyzed using a gas chromatograph (TCD type). H₂ permeation measurements were performed over 300°C, 50-100 kPa with H₂ and helium (He) mixture on the primary side. The measured H₂ permeability of the composite membrane was the same order as one of the reported values. The H₂/He selectivity in the permeated gas values were in the range of 300–2000 for measurements; therefore, it was assumed that the effect of membrane pinholes on H₂ permeation flux measurements was negligible. As a result of a long-term H₂ permeation operation test at 320°C, durability was confirmed for 144 hours with the selectivity of over 300. From an SEM image of the cross-section that the membrane after the H₂ permeation tests, the membrane displays a two-layered structure comprising a Pd₆₀Cu₄₀ layer and a porous Ni layer. And the absence of delamination indicates high adhesion between the layers. The performance of the proposed composite membrane was compared with that of a pure Pd₆₀Cu₄₀ membrane prepared according to a conventional rolling method. The Pd required amount of the composite membrane was less than 1/8 for a rolled Pd₆₀Cu₄₀ one for the same amount of H₂ permeation.

CONCLUSION: To achieve high-capacity H₂ separation, this study demonstrated the production of a porous Ni layer for the reverse build-up method to fabricate an H₂-permeable membrane that can be formed into a flat plate. A Ni-supported, Pd₆₀Cu₄₀ membrane with a 3.7- μ m-thick Pd₆₀Cu₄₀ layer and 13- μ m-thick porous Ni layer was prepared. Subsequently, the H₂ separation performance of the membrane was investigated. From the results, it was demonstrated that the membrane method had cost benefits in comparison with the conventional metallic rolling method. It was clarified that further thinning of the Pd₆₀Cu₄₀ layer can further reduce the required amount of Pd. With this technology, it may be possible to fabricate a large-area, flat-plate, H₂-permeable membrane at a lower cost than the conventional rolling method for high-capacity H₂ separation.

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TECHNO-ECONOMIC EVALUATION OF BRAYTON BATTERY CONFIGURATIONS WITH POWER-TO-HEAT EXTENSION

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Utility-scale Electrical Energy Storage (EES) supports the expanding integration of intermittent renewable energy sources allowing a reliable and flexible supply of low-carbon or even zero-carbon electricity. Emerging EES technologies such as Carnot Battery, CAES and LAES are considered adiabatic due to the implementation of thermal energy storage (TES) following the adiabatic compression during the Carnot heat pump cycle and prior to the adiabatic expansion during the Carnot heat engine cycle. Such adiabatic technologies are able to conserve electric energy with a theoretical round-trip efficiency of 100%. For economically promising adiabatic concepts, such as CAES and Brayton Battery, cost estimations indicate Levelized Costs of Storage (LCOS) of less than 150 €/MWh. However, these costs are still too high for an economical operation in future electricity transmission systems.

The large-scale conversion of electricity into thermal energy using an isobaric heating process with subsequent conservation inside TES is an inexpensive method for increasing the energy density of the overall process. Such an integration of Power-to-Heat (PtH) towards a partial adiabatic operation management decreases the round-trip efficiency on the one hand, but, opens up the potential for cost reduction on the other hand. The objective of this contribution is to quantify this trade-off between the energy efficiency and cost efficiency for a Brayton Battery configuration. To this end, a wide-range simulation study with integrated PtH source is performed. In addition to the thermodynamic analysis, an economic assessment of advanced Brayton Battery configurations is presented.

This techno-economic assessment illustrates the benefits of the PtH integration inside a Brayton Battery. The results show a significant reduction of specific capital costs by up to 10% for increased integration of electrical heating capacity through PtH, which is accompanied by a higher system flexibility and a slight loss in round-trip efficiency.

Concludingly, the implementation of PtH during the charging mode is an inexpensive option to increase the storage density and thus decrease the capital costs of the overall system.

Ni-DOPED CDS QUANTUM DOTS SENSITIZED 3D ROSETTE-ROD TiO₂ PHOTOANODES FOR PHOTOELECTROCHEMICAL WATER SPLITTING

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INTRODUCTION: Hydrogen is considered as the ultimate clean energy source because of the current socio-economic and environmental circumstances[1]. It is considered as an efficient energy vector that can be produced, transported, stored and consumed utilizing distinctive courses. Currently, 95% of hydrogen is mostly produced from fossil fuels, like steam reforming. However, hydrogen production from renewable sources is not that quite popular because of high cost and low efficiency. Therefore, it has been highly recommended to develop highly efficient and green routes to produce hydrogen. Photoelectrochemical (PEC) water splitting is considered a cost-effective and promising technique for sustainable hydrogen production with using solar energy [2]. Herein, we fabricated 3D rosette-rod TiO₂ photoanodes sensitized with Ni-doped CdS quantum dots (QDs) using hydrothermal and successive ionic layer adsorption and reaction (SILAR) approach.

MATERIALS AND METHODS: Initially 1D TiO₂ NRAs were grown on FTO glass substrate using hydrothermal method which were then used as a substrate for 3D rosette-rod TiO₂. Briefly for 1D TiO₂ NRAs a transparent mixed solution consisting of 30 mL of HCl (37 %), 30 mL of distilled water and 1 mL of Ti(OC₄H₉)₄ was transferred to teflon lined steel autoclave provided with FTO substrate and hydrothermal reaction was carried out at 150 °C for 12 hours. The FTO substrate with 1D TiO₂ NRAs grown over them were then taken out washed, dried and calcined at 500 °C for an hour. To convert these 1D TiO₂ NRAs into 3D rosette-rod TiO₂ two-step hydrothermal approach was used. The prepared 1D TiO₂ NRAs were placed in a Teflon lined autoclave containing 0.4 M aqueous TiCl₄ solution for an hour at 100 °C to obtained a densely TiO₂ seeded 1D TiO₂ NRAs. These densely seeded 1D TiO₂ NRAs were then converted into 3D rosette-rod TiO₂ by using a transparent mixed solution of 30 mL of HCl (37 %), 30 mL of distilled water and, 0.6 mL of TiCl₄ inside a teflon lined autoclave. Hydrothermal reaction was then carried out at 150 °C for 3 hours. Finally, 3D rosette-rod TiO₂ photoelectrode were taken out cleaned with distilled water and ethyl alcohol and were calcined at 500 °C for an hour. Pristine and Ni-doped CdS QDs were deposited on 3D rosette-rod TiO₂ using SILAR method. 3D rosette-rod TiO₂ were exposed to Cd²⁺ and S²⁻ ions by successively dipping in their respective solutions of Cd(NO₃)₂·4H₂O, and Na₂S·9H₂O. Anionic and cationic precursor aqueous solution consist of 0.1 M Cd(NO₃)₂·4H₂O and 0.1 M Na₂S·9H₂O. Deposition involves dipping of 3D rosette-rod TiO₂ photoanode separately into Anionic and cationic precursor solution and washing in between them with distilled water to remove extra and loosely attached ions. Immersion time of photoanode is 5 minute for both Anionic and cationic precursor solution with 30 Second rising time in distilled water after each immersion. This complete four step cycle is termed as 1 SILAR cycle. To Synthesized Ni²⁺ doped CdS QDs required concentration (5 mM, 10 mM, 25 mM, and 50 mM), of Ni(CH₃CO₂)₂ added to the Cd(NO₃)₂·4H₂O solution. Photoelectrode surface morphology, crystal structure and solar light absorption were investigated with SEM, XRD and Uv-vis spectrometer. Photoelectrochemical performance of photoanodes was investigated with linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and Chronoamperometric measurements under simulated 100 mW/cm² solar light irradiations. PEC measurements were carried out with conventionally a three-electrode cell including Ag/AgCl (3 M KCl) saturated electrode as a reference electrode, photoanodes act as a working electrode and while a Pt sheet as a counter electrode. An aqueous mixed solution of 0.1 M Na₂SO₃ and 0.1 M Na₂S (pH ≈ 12) was employed as an electrolyte.

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RESULTS: FESEM images consist of two different kind of nanostructure exist simultaneously in 3D rosette-rod TiO_2 , one dimensional TiO_2 nanorod arrays present at the bottom, while three dimensional nano rosette consisting of small TiO_2 nanorods as building units at the top. CdS Ni doped CdS QDs were found to be uniformly deposited not only on the tip but also on the side surface of the nanorods that establish the nano rosettes structure. Uv-vis spectra shows with deposition of Ni-doped CdS QDs the absorption edge is shifted toward the visible region from 410 nm to 520 nm and an enhancement in the visible light absorption have been observed with increase in Ni concentration. Among various concentration Ni dopant concentration 25 mM from LSV result shows the highest photocurrent density of 1.106 mA cm^{-2} at 1.2 V vs. NHE. While pristine 3D TiO_2 photoanode shows the maximum photocurrent of 0.52 mA cm^{-2} . Chronoamperometric measurements demonstrates that among all the photoanodes 25 mM concentration Ni-doped CdS QDs on 3D TiO_2 shows the highest photoresponse.

CONCLUSION: 3D rosette-rod TiO_2 nanorods were effectively fabricated over 1D TiO_2 NRAs using two steps hydrothermal approach. Uv-visible results indicate that proper Ni^{2+} doping enhances light absorption in the visible region of the solar spectrum. 25 mM Ni doped CdS QDs, shows the highest performance for photoelectrochemical water splitting.

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COUPLING OF BUILDING SIMULATION WITH REAL TIME MEASUREMENTS OF PCM COMPONENTS - A HARDWARE IN THE LOOP APPROACH

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INTRODUCTION: Building components with phase change materials for latent heat storage are coupled in the application with the building thermal management system and with the building itself. Therefore, the dynamic performance of the PCM components cannot be tested separately, without taking into account the interaction with the building and its thermal management system. Consequently, the PCM components have to be tested in test rooms, in order to get information about their performance in the application. The installation and monitoring of test rooms is complex and expensive. An alternative approach are sophisticated building simulations. However, with the purely simulation-based approach, there are still difficulties in the realistic modeling of PCM components, which also take into account special characteristics such as supercooling and time-varying phase fronts. Therefore, a hardware in the loop setup was developed, where a building simulation is coupled with real time measurements of PCM components. This enables the interaction of the components with the system during the measurement without the need to install the complete system. On the one hand, the hardware in the loop approach provides extreme flexibility in the characterization of PCM components in the application and, on the other hand, ensures very reliable results.

MATERIALS AND METHODS: The hardware in the loop setup consists of a measurement setup with which the temperatures and heat flows of the PCM sample can be recorded. This setup is connected to a building simulation model in the software Trnsys 18. The measured and simulated data are exchanged in real time using a Python-Labview interface and thus the interaction of the sample with the building is established. The investigated specimen is a macro encapsulated and shape stabilized PCM for the application in the building envelope. Boundary conditions for the simulations are measured weather data. This allows a comparison with outdoor measurements on a mock-up of the entire facade element containing the PCM for validation purposes.

RESULTS: By coupling the measurement of a PCM component with a building simulation, their interaction can be investigated. The measurements of the hardware in the loop setup show good agreement with the measurements in the outdoor measurement setup on the facade element mock-up.

CONCLUSION: The coupling of building simulation with real time measurements of PCM components in a hardware in the loop setup provides an extremely flexible characterization method and at the same time enables the virtual interaction of the investigated sample with the system in application. The approach is a step towards faster component testing under application conditions and makes the setup of test rooms obsolete in many cases.

TECHNO-ECONOMIC ASSESSMENT OF THERMAL ENERGY STORAGE SYSTEMS FOR SMALL-SCALE CSP PLANTS RUNNING ORGANIC RANKINE CYCLES

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Small-scale concentrated solar power (sCSP) plants represent an attractive alternative to power production in remote areas with sufficient solar radiation. In order to reduce the capital investment, these plants are commonly equipped with Linear Fresnel collectors and organic Rankine cycles (ORC). This combination provides greater operation flexibility compared to other concentrating technologies coupled to steam Rankine cycles. To improve the sCSP plant dispatchability, a thermal energy storage (TES) system is recommended. One example is the demonstration sCSP plant installed in Ben Guerir (Morocco), with a linear Fresnel solar field of 4,900 m² and a power block capacity of 1 MWe. After its construction, the plant was updated to include a TES system in the framework of the ORC-Plus project (H2020).

The work presented in this paper addresses the techno-economic viability of the TES system constructed in this sCSP plant, that is based on packed bed technology. For this purpose, a model has been developed based on the TRNSYS platform. Specific subroutines (Types) have been developed for the key plant components, i.e. ORC power block, linear Fresnel collectors and packed bed. While for the rest of equipment and systems, models from TRNSYS library have been considered. Special attention has been taken in the development of the packed bed model and its validation with experimental data obtained in a 1:100 prototype constructed at CIC energiGUNE facilities. This prototype uses the same filler material (Magnetite ore) and heat transfer fluid (Delcoter Solar E15 thermal oil) as the TES tank constructed in Ben Guerir.

Annual operation simulations have been run for the original plant (linear Fresnel solar field, ORC power block, valves, pumps, piping and controlling system) and for the new configuration (extension of the solar field and TES system). Besides, the selected novel TES solution is compared with the well-known double tank technology. This comparison is mainly focus in two directions. On the one hand, in the lower capital investment of the packed bed system associated to the use of a single tank instead of two and in the implementation of a low-cost TES filler material. And, on the other hand, in one of the main drawbacks of the packed bed systems, the temperature drop generated in the discharge operation when the thermocline region is extracted from the TES and its direct effect in efficiency loss in the power block.

Overall, the obtained results show the possibility of extending the annual electrical production of the plant in up to a 40% by implementing the proposed TES system. Furthermore, even though the aforementioned drawback of the packed bed technology, the obtained results show the economic benefits of this TES technology when compared to a double tank system.

MODELING PHASE CHANGE MATERIALS IN ADVANCED URBAN CANOPY MODELS

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INTRODUCTION: Increasing anthropogenic heat sources, and other urban fabric attributes, are strongly modifying urban microclimate conditions as demonstrated by means of satellite measurements, field monitoring and modelling at mesoscale and canopy layer scale. Despite the very promising results of such methods, they mostly remain diagnostic and prognostic. What remains missing are prescriptive models aimed at better designing building envelope dynamic characteristics within the investigated urban environment. In particular, the influence of novel materials with thermal-energy performance that varies during the course of daily and seasonal fluctuations is missing even from the most sophisticated models.

MATERIALS AND METHODS: Among these adaptive solutions, phase change materials (PCMs), represent a fairly promising application to be examined. The effect of PCMs at component and single building level has been widely investigated through local observations and models, yet, their influence at a larger scale remains poorly understood. In this work, the governing equation of the solidification/melting latent energy storage process was integrated within the complex framework of the Princeton Urban Canopy Model (PUCM). In this way, the model was equipped with a dedicated numerical application that allows to represent the effect of a layer of phase change materials with different thicknesses and variable thermo-physical properties. The modified PUCM was used to run year-long simulations and compare the effect of three different PCMs integrated in the walls of the canopy buildings. These PCMs were characterized by a melting temperature of 20, 24, and 28 °C and a fixed latent heat of fusion of 180 kJ/kg.

RESULTS: Results show that the numerical representation of the PCMs could be effectively integrated in the PUCM code. This integration allowed to successfully quantify the effect of PCMs in terms of internal and external surface temperature for the building walls in the selected canopy. Additionally, the effect of PCMs in terms of canopy air temperature was also calculated for each of the selected scenarios. The selected melting temperature is found to have a crucial role in the final buffer effect of the latent application. For this reason, the use of Urban Canopy Models could represent an enhanced method optimization of building integrated PCM-based applications for passive cooling and heating purpose.

CONCLUSION: The obtained results demonstrate that PCM can effectively be embedded in urban canopy models and that the modified UCM can be used to investigate the effect of phase change processes in complex building stratigraphy.

AN ALGORITHM FOR OPTIMAL SELECTION OF THERMAL ENERGY STORAGE OPTIONS IN INDUSTRIAL WASTE HEAT RECOVERY APPLICATIONS

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INTRODUCTION: The selection of the most suitable thermal energy storage in waste heat recovery applications is a challenging task. It involves several variables related to choice of the storage material and layout, which highly impact on the recovery from the heat source and the load operation and performance.

MATERIALS AND METHODS: An original algorithm is proposed in this work based on seven consecutive steps which lead to the selection of the best material and storage design for the given waste heat source and heat utilization/conversion system. The algorithm is first presented for sensible thermal energy storage and it is then generalized to address the best integration of latent heat and thermochemical energy storage. It consists of a preliminary design step to calculate the storage design, material and inventory and a simulation step to evaluate the transient response of the system in the charging and discharging processes. The functional parameters of the storage are selected to maximize the amount of waste heat recovered and not to degrade its quality. In the discharging the main outputs are the time variation of the temperature of the heat transfer fluid heated by the storage medium and the thermal power transferred to the load. If these values enable a proper and efficient operation of the load (e.g. domestic water heater, space heating, process heat for industrial processes, heat-to-power systems, heat upgrade systems, etc.), then the storage selection can be considered successful. The application of the algorithm is demonstrated for waste heat recovery from a discontinuous industrial process and utilization in a heat to power conversion system taking into account both consolidated and advanced storage options.

RESULTS: The results show how the electricity generated by the integrated system embedding the optimized storage design is highly improved compared to a more traditional choice. Moreover, the impact on the economics of the overall system is analysed.

CONCLUSION: The algorithm presented can therefore be used as an effective tool for choosing among thermal storage options in waste heat recovery applications.

GIGA SCALE PIT STORAGE AS AN ESSENTIAL PART OF DISTRICT HEATING SYSTEMS

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INTRODUCTION: Due to the fluctuating nature of renewable heat sources, thermal energy storage (TES) is a necessary technology needed to bridge the gap between supply and demand in the heating sector. For district heating networks, large-scale TES technologies such as pit and tank storages have proven to be well suited for this. Such storages have already been constructed in Denmark with volumes up to 200,000m³. The gigaTES project focuses on the development of pit storages in the range of 100,000- 2,000,000m³ in storage design, construction, and integration of such storages on DH grids.

MATERIALS AND METHODS: A significant part of the project focuses on a detailed simulation study of giga scale TES technologies integrated as part of representative case studies in Austria (e.g. Vienna, Salzburg). As Austrian DH grids typically operate at higher system temperatures than their Danish counterparts, the application of additional post heat sources (heat pumps or heating plants) needs to be considered and evaluated.

The goal of a series of scenario studies is was optimise the integration and operation of a giga scale pit storage as an element in the overall DH supply mix, preferably at the highest ecological benefit and at the lowest possible cost. Thus, technical, ecological and economic indicators are used to assess the overall system performance. Detailed simulation results for a number of scenarios based in Vienna will be presented which aim to increase the utilisation of an nearby geothermal heat source at the lowest overall cost. A variety of locations were considered, one of which makes use of a low temperature secondary network to avoid any post heating as well as more challenging scenarios where the storage will supply the primary grid through assistance of a high temperature heat pump or through mixing with the outlet of nearby heating plants. The impact of varying the storage capacity, depth, and insulation on the levelized cost of heat and overall grid CO₂ savings are investigated in a parameter study for each application scenario subject to the boundary conditions of the grid. Suitable storage configurations are identified and presented in more detail. The system modelling was carried out in Dymola/Modelica using both existing and new component models developed within the scope of the project.

RESULTS AND CONCLUSIONS: The parameter study results identify a range of potential storage designs ranging from €30/MWh to €80/MWh achieving varying degrees of CO₂ savings depending on their mode of operation and location. Post heating remains a difficult challenge for pit storage integration in high temperature grids when trying to avoid any additional CO₂ emissions in the process. Availability of nearby high temperature, carbon free heating sources or advancements in large scale, high temperature heat pump technologies prove to be important factors to consider when choosing a location for such large scale storages.

EXPERIMENTAL STUDY OF ETTRINGITE MATERIALS FOR THERMOCHEMICAL ENERGY STORAGE IN BUILDINGS

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A high-efficiency system of thermochemical energy storage (TCES) is one of the most promising technologies to meet the high demand for thermal energy all-around year in buildings. This kind of solution needs a good candidate TCES material, of which the energy storage density should be as high as possible but also at the low material cost. Recent investigations on ettringite demonstrated its potentiality in the large scale of TCES because of no-toxicity, low material cost, and high energy density at lowing operating temperature, etc.

In this study, the thermochemical properties of pure ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 30.6\text{H}_2\text{O}$, instead of $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$ for theoretical chemical composition) and the relevant reaction mechanisms were first investigated during the hydration/dehydration processes (formation of ettringite/meta-ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot n\text{H}_2\text{O}$, $n\leq 12$)). The energy storage/releasing density of ettringite was as high as 536 kWh/m³. The reaction kinetics and thermodynamics demonstrated stepwise transformations of different hydration states under isothermal and isobaric conditions:

- Dehydration: $\text{Ett}_{30.6} \rightarrow \text{Ett}_{30} \rightarrow \text{Met}_{12} \rightarrow \text{Met}_6$, bivariant at $> 50\text{ }^\circ\text{C}$;
- Hydration: $\text{Met}_{7.4} \rightarrow \text{Met}_{12} \rightarrow 24\text{-hydrate} \rightarrow \text{higher hydrates}$, an alternative process between bivariant and monovariant).

Where Ett_X ($X=30.6, 30$) means ettringite crystals containing $X\text{ H}_2\text{O}$ molecules, Met_Y ($Y=6, 7.4, 12$) represents meta-ettringite containing $Y\text{ H}_2\text{O}$ molecules.

In order to avoid the agglomeration of ettringite powder during rehydration, a cement-based ettringite composite (70 wt% ettringite, without any supplementary holding matrix material) was developed in view of the investigation on carbonation failure mechanism of ettringite. It has been proved that ettringite was carbon resistant during the material storage period under ambient conditions if being applied for long-term thermochemical energy storage. However, it would be destructed to small molecules, like gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$) or semi-hydrate ($\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}$), vaterite and aragonite (CaCO_3 polymorphs), aluminum hydroxyl, during the rehydration in humid environment that containing CO_2 . The corresponding energy storage capacity would be decreased, from 282 kWh/m³, proportionally to the bound CO_2 content. This work made it possible to deduce some relevant information as to their durability in terms of their use in TCES.

This developed ettringite composite material was then characterized for its thermal performance in an open-mode fixed bed reactor (56 mm high porous bed composed of granules of 1–2 mm in diameter). The energy charging/discharging process carried out to study the reversibility of ettringite/meta-ettringite under various operating conditions. Accompanying a very rapid response in several seconds, the maximum instantaneous power was as high as 915 W per kg of original ettringite composite with the maximum temperature lift of 37.5 °C. The energy-releasing capacity was 176 kWh/m³. These promising results will be very useful to design a future prototype (in scale 1:1) containing ettringite materials for a heating system in buildings.

IMPACT OF Fe- AND La-DOPING ON THE THERMOCHEMICAL HEAT STORAGE CAPACITY OF CaMnO_3

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INTRODUCTION: Recently, perovskites (ABO_3) have been considered promising candidates for high-temperature ThermoChemical heat storage (TCS) applications through oxygen exchange reactions. The amount of chemical heat stored per kg of material, or chemical heat storage capacity, is given as $Q(\text{kJ/kg})=1/M \int \Delta h \, d\delta$, where M is the molar mass of the material, Δh (kJ/mol) is the enthalpy of reduction associated with the redox-reaction integrated between δ_i , the initial oxygen non-stoichiometry, and δ_f , the non-stoichiometry at a final condition of interest. From this equation, it is evident that the larger the reaction enthalpy (Δh) and extent ($\Delta\delta = \delta_f - \delta_i$) are, the larger would be the heat storage capacity. In reality, since the reaction enthalpy corresponds to the energy associated with the generation of oxygen vacancies, the higher is the reaction enthalpy (the more difficult is the material to be reduced/oxidized), the smaller is the reaction extent. Therefore, it is fundamental to find an optimal compromise between the two metrics, reaction extent, and enthalpy. In perovskites, the thermochemical behavior of the material can be tuned by doping. In this study, the impact of Fe- and La-doping on the thermochemical properties of CaMnO_3 are investigated. We carry out here a thermodynamic study and comparison of these oxides under temperatures and oxygen partial pressures of relevance to high-temperature TCS applications. The thermodynamic data enable evaluation of the heat storage capacity for any set of desired cycling conditions.

MATERIALS AND METHODS: The thermochemical behavior (reduction/oxidation cycles) of the $(\text{La}_x\text{Ca}_{1-x})(\text{Fe}_y\text{M}_{1-y})\text{O}_3$ oxides (dopants content 10-30% at. in either A or B sites) was investigated under a wide range of conditions (i.e. $p\text{O}_2$ range 0.18-0.008 atm, temperature range 400-1200 °C) by thermogravimetric (TG) analysis. The reaction enthalpy (Δh) of characterized compositions was evaluated applying the van't Hoff approach to the TG data in the Arrhenius form ($\ln(p\text{O}_2)$ vs. $1/T$) at specified values of oxygen non-stoichiometry change (δ).

RESULTS: It is found that La doping increases the reduction enthalpy (Δh) (~195 and 189 kJ/mol, respectively for LCM10 and LCM30) with respect to CM (~167 kJ/mol), but the reduction extent decreases significantly as the dopant amount increases. This leads to an overall decrease in the heat storage capacity of the La-doped materials with respect to CM (~272 kJ/kg): ~256 and 92 kJ/kg for LCM10 and LCM30, respectively. In contrast, Fe-doping increases the reaction extent relative to CM. At the lower dopant level (CMF10), due to similar reaction enthalpy with respect to CM (~182 kJ/mol) the wider $\Delta\delta$ results in an increase in the heat storage capacity (~344 kJ/kg). While in the more heavily doped material (CMF30) the enthalpy of reduction is lower (~161 kJ/mol) than in the reference system. Consequently, despite the similarity in reaction extent, CMF73 offers a lower heat storage capacity (~221 kJ/kg) than CM and CMF91.

CONCLUSIONS: In this study, the impact of Fe- and La- dopants on the thermochemical properties of CaMnO_3 has been investigated. CMF10 material showed higher heat storage capacity and can be considered a promising candidate for high temperature (400-1200 °C) thermochemical heat storage application.

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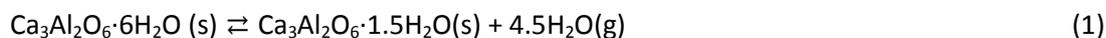
SYNTHETIC STRATEGIES FOR THE ENHANCEMENT OF TRICALCIUM ALUMINATE HEXAHYDRATE HYDROTHERMAL CYCLING PERFORMANCES

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INTRODUCTION: in the field of thermochemical storage materials (TCMs), the development of tricalcium aluminate hexahydrate ($\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$, known as katoite) based materials represents a new challenge. Suitable features as high hydration heat (-522.8 kJ/mol) and dehydration temperature between 200 °C and 300 °C, make the applicability of $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ more effective than conventional materials operating at medium-temperature. The cyclic medium-temperature reactions could be schematized as follows (eq.1):



However, pure katoite shows low chemical stability during the cycling, in fact a decomposition into mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) and calcium oxide (CaO) leads the material to be less efficient after few cycles. On the other hand, in correspondence with the formation of CaO, which is subsequently hydrated to hydroxide, the material seems to be stabilized thanks to the new surface basicity conditions. In this purpose, aim of the work is the evaluation on the effect of calcium hydroxide addition on katoite materials, by studying different $\text{Ca}^{2+}/\text{Al}^{3+}$ molar ratios, thus optimizing the features of the newly synthesized materials, in order to find a good compromise amongst cycle stability, heat efficiency and storage density.

MATERIALS AND METHODS: investigated materials were prepared by co-precipitation synthesis method in aqueous solution. Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) provided the metal cations in solution and sodium hydroxide (NaOH) as hydroxyl ions source was added. All the samples were subsequently treated at 1100 °C for 2 h in air and then hydrated under accurate conditions in a hermetic closed system. The materials characterization concerned a structural and morphological investigation (by means of X-ray diffraction and scanning electron microscopy analysis) and a thermochemical investigation (by means of thermogravimetric and differential scanning calorimetry analysis). The cycling tests were carried out by a thermogravimetric system coupled with a water vapour generator, able to create the conditions of a hydrothermal cycle.

RESULTS AND CONCLUSION: the preliminary results showed that, using a 3:2 $\text{Ca}^{2+}/\text{Al}^{3+}$ initial molar ratio, the co-precipitated product presented a final $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}/\text{Ca}(\text{OH})_2$ ratio of 8:1. In terms of thermochemical performances, a dehydration heat of 655.8 kJ/kg was reached, lower than the pure katoite one (807 kJ/kg). Although the less storage capacity, after hydrothermal cycling $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}/\text{Ca}(\text{OH})_2$ hybrid material showed an improvement of +22% in terms of stored/released heat per mass unit after the structural stabilization occurred (three cycles needed). Additionally, the XRD phase identification highlighted no presence of katoite decomposition products, with respect to pure $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$. Given the low cost of the studied material and the possibility of easily intervening on the synthesis methodology to improve its cycling performances, tricalcium aluminate hexahydrate can be considered a promising material for applications in TES.

DEVELOPMENT OF $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ ($0 \leq x \leq 1$) MATERIALS FOR THERMOCHEMICAL ENERGY STORAGE AT LOWER RED-OX TEMPERATURE

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INTRODUCTION: Thermal energy storage (TES) systems will play a major role for renewables integration as well as to increase the energy efficiencies in industrial processes in the world transition to a decarbonized energy system [1]. One of the most promising TES technologies is thermochemical energy storage (TcES), counting with the highest theoretical energy density [2]. The most promising materials are cobalt oxide ($\text{Co}_3\text{O}_4/\text{CoO}$) and manganese oxide ($\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$) [3], but their high equilibrium reaction temperatures makes them not suitable for their application in CSP. This research is focused on the development of advanced pure mixed oxides with lower Red-Ox temperatures than Co_3O_4 . In fact, a solid solution between cobalt oxide and nickel oxide with the general formula $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ ($0 \leq x \leq 1$) is developed.

MATERIALS AND METHODS: The solid solution has been synthesized by sol-gel method with the formula $\text{Co}_{3-x}\text{Ni}_x\text{O}_4$ ($0 \leq x \leq 1$) following the Pechini route. X-Ray powder diffraction (XRD) measurements have been done to study the composition and the cristalinity of the sample and the Red-ox temperatures have been assessed by thermogravimetical analyses (TGA).

RESULTS: The room temperature XRD patterns confirm that the materials with an increasing amount of nickel (x) from 0 to at least 0.6 have similar patterns with continuous changes in the form and the position of the peaks. However, when the amount of nickel is higher ($x \geq 0.8$) the patterns show peaks characterizing the presence of Nickel monoxide (NiO) as impurity. The thermal behaviour of the materials has been assessed by TGA determining the Red-Ox temperatures, reaction reversibility and stability during cycling. Regarding the reaction temperatures, results show a significant decrease in them when nickel is present in the mixed structure, making it tunable. The reduction temperature has an almost linear decrease when the nickel content (x) varies from 0 to at least 0.6, but when it is higher ($x \geq 0.8$), the reduction temperature does not follow the trend. This phenomenon may be due to no formation of the right stoichiometry of these materials as a nickel oxide phase was detected as impurity. The cyclability test of the materials show that for the materials with a nickel content (x) from 0 to at least 0.8, the reduction took place upon heating which is evidenced by the sample weight loss related to oxygen release and the re-oxidation took place evidenced by the weight gain upon cooling. When $x=1$, there were minor weight losses and gains during cycling indicating that the material was not reversible. The thermal stability test shows a complete reversibility and maintains similar reduction temperature.

CONCLUSIONS: The results confirm good thermal stability and good performance of these materials which makes them potential candidates for TcES applications at high temperature.

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THERMOCHEMICAL STORAGE OF LOW-TEMPERATURE WASTED HEAT BY ORGANIC SALT HYDRATE MATERIAL

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INTRODUCTION: In every kind of process, a fraction of energy involved is irremediably lost as heat [1], but thermal energy storage (TES) systems, which accumulate thermal energy to use it on demand, may be a compelling way to benefit from such waste energy. Among such systems, those based on the storage of thermochemical energy are particularly interesting because the high value of collected energy and the low heat losses [2][3]. For this purpose, hydrated salts resulted to be the most performing materials for a thermal storage at mid-low temperatures. The thermal energy is accumulated by a dehydration process (endothermic) and released through a hydration process (exothermic) [4].

MATERIALS AND METHODS: To the best of our knowledge, all the salt hydrates studied so far are composed by inorganic ions and, often, they suffer deliquescence phenomena that compromise their efficiency [5][6]. This work is, instead, focused on the study of organic salt hydrates, solving the deliquescence issue by using compounds highly insoluble in water; in particular, our attention focused on a calcium ceftriaxone salt, with the purpose to obtain a dehydration/hydration reversible reaction with an equilibrium temperature lower than 100 °C. The thermochemical behaviour of the compound was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), analysing the thermal stability and the reaction enthalpy involved in relation to the progression of the dehydration/hydration cycles.

RESULTS AND CONCLUSIONS: From obtained data, calcium ceftriaxone shows a dehydration process centred at about 100 °C that involves six water molecules. Considering the mean value of enthalpy associated to such process (53.8 kJ per mole of H₂O), which is comparable to the values regarding the well-known inorganic salts [4], Calcium ceftriaxone, at least from a thermodynamic point of view, is an excellent candidate as material for thermochemical energy storage and it supports the use of other still-to-study hydrated organic salts for this kind of application.

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INDUSTRIAL BYPRODUCTS CHARACTERIZATION FOR HIGH TEMPERATURE SOLID PARTICLE SOLAR TOWER SYSTEMS USED AS THERMAL ENERGY STORAGE AND HEAT TRANSFER FLUID

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INTRODUCTION: Power generation from renewables had become a major source of energy during the last decade. Even during 2020 world crisis has continued to grow showing a remarkable resilience [1]. Solar Concentrating Solar Power (CSP) electricity generation has shifted quickly from 2 TWh generated in 2010 with 1 GW of power into 15 TWh in 2019 with 6 GW of power. It is projected to grow up to 788 TWh and 253 GW of power in the next 20 years in a sustainable policy scenario [1]. Initially Spain and US led the current installed capacity, but recently new additions had been made by other countries such as China, South Africa, Israel, Chile, Kuwait, United Arab Emirates, among others. Almost every new addition includes thermal energy storage in order to get more competitive [2,3]. Levelized cost of energy from CSP continued to decline and it is expected to continue in this way [2,4]. New large-scale CSP additions under development are mostly solar towers which are being installed in China and in Middle East countries [4].

Current state-of-the-art CSP commercial technology uses molten salts as Heat Transfer Fluid (HTF) and Thermal Energy Storage (TES) media [5–7]. However, molten salts service temperature limitation prevents a more efficient heat to power conversion since they become unstable at temperatures over 565 °C [8]. New CSP tower generation had been under development in recent years. Most promising technology under development is the one that replaces the use of molten salts with solid particles material which can overcome molten salts drawbacks at temperatures over 565 °C [9–11]. Until now, material characterization and selection has been focused on natural raw materials and synthetic ones [12–17].

In addition, current efforts for improving global sustainability had evolved to circular economy industrial system development in which material resources are used as long as possible within different economic activities [18]. Among different disposal of waste materials that cannot be recycled, reuse is one of the desirable ways to re-enter these materials into a new life cycle and improve its circularity [19,20]. Therefore, considering industrial waste and byproducts for new technology applications is necessary to help with this economy paradigm change [21].

BYPRODUCTS AND CHARACTERIZATION: In current study, different by-product granular materials had been identified from several energy intensive industrial processes that use temperatures above 1000 °C. These materials were characterized as previous natural and synthetic materials had been characterized for use as solid particle material to be used as HTF and TES material for new generation CSP tower applications. Materials under study included are grey slag, black slag, steel mill dust, and gossan. Grey slag comes from blast furnaces of steel industry, it contains mainly silicates and calcium oxides [22]. Black slag is a byproduct produced in electric arc furnace used in steel industry, it is formed primarily by iron oxides and calcium oxides [23]. Steel mill dust is recovered from smelting furnace gases and contains high density metal oxides such as zinc monoxide and iron trioxide [24]. Gossans contain high levels of SiO₂ and iron, it can be obtained from copper industry [25].

In this study thermal stability was studied by evaluating the effect of high temperature in the long term of the granular materials. Samples were analyzed as-received, after 300 hours at 900 °C and after 500 hours at 900 °C. Characterization techniques used for properties and parameter determination were: solid density with a helium pycnometer, Particle Size Distribution (PSD) by laser diffraction detection, specific heat capacity with a Differential Scanning Calorimeter (DSC), thermal stability by a Thermogravimetric Analysis

(TGA), solar absorptance with a spectrophotometer with integrating sphere, chemical composition with X-Ray Diffraction (XRD), and optical examination using Scanning Electron Microscopy (SEM).

RESULTS: Most relevant results of this study are presented. Solar absorptance of grey slag and black slag remained stable during the thermal aging test, remaining in 65% and 85% respectively. For gossan, solar absorptance increased almost to 80% from 65.8% in the first 300 hours of thermal treatment and then decreased to 77.2%. Meanwhile, steel mill dust decreased its solar absorptance from 93.1% to 64.2% after 300 hours and remained stable up to 500 hours (Figure 1a). Specific heat capacity results can be observed in Figure 1b). Gossan have the lowest specific heat capacity. However, it had a slight increase to get over 1 J/h·K. On the other hand, steel mill dust had a slight decrease during the thermal treatment. Black slag and grey slag showed almost not changes in this matter.

Figure 1. a) Solar absorptance for gossan and steel mill dust as-received, after 300 hours and after 500 hours at 900 °C. b) Specific heat capacity changes of steel mill dust, grey slag, black slag and gossan at 900 °C

SEM images show that black slag remain stable Figure 2a) and 2b), even that PSD shows a small decrease in bigger particles and an increase in small size particles. This behavior is presented by all the materials with the exception of Gossan (Figure 2c) in which PSD shows signs of sintering.

Figure 2. a) SEM of black slag as-received. b) SEM of black slag after 500 hours at 900 °C. c) PSD of gossan as-received, after 300 hours and after 500 hours at 900°C

CONCLUSIONS: Gossan can be interesting because it changes increasing solar absorptance and specific heat capacity. However, security due to toxicity of the material should be taken into the account into the plant financial balance and into the risk assessments. Black slag is the most promising of the materials due to favorable properties and parameters and thermal stability in the long-term. Grey slag shows thermal stability but its low solar absorptance make it more adequate for indirect solar radiation systems. Steel mill dust decrease of properties and parameters shows that it's not acceptable due to the high temperature effect in the long term. Further studies must be made to ensure the behavior of these materials, such as composition stability from different industrial sources and combined thermal cycling tests.

THE ENABLING ROLE OF NANOPARTICLES IN THE DEVELOPMENT OF ANTICORROSION COATINGS FOR MOLTEN SALTS THERMAL ENERGY STORAGE APPLICATIONS

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INTRODUCTION: Molten salts based thermal energy storage (TES) systems have demonstrated their feasibility at industrial level in concentrated solar power (CSP) plants. Doping of these molten salts with nanoparticles has attracted major interest, aiming to achieve nanofluids with enhanced thermophysical properties, such as thermal conductivity and specific heat, which would result in an efficiency increase and a cost reduction of the CSP plants. Moreover, recent studies have shown that nanoparticle addition also affects the corrosivity of the base fluid. However, while some works confirmed a marked corrosivity reduction for solar salt (NaNO₃ 60%wt.–KNO₃ 40%wt.) based nanofluids [1-4], other cases based on HitecXL presented a negative effect on the corrosion behavior [5,6]. In spite of this difference, all the studies corroborated the incorporation of nanoparticles into the corrosion layer, which explains the corrosion behavior modification. This incorporation of nanoparticles in a metallic matrix has been also studied by molecular dynamic simulations [7].

In this presentation we review the latest progress in molten salts nanofluids corrosion and demonstrate how it can be used to develop anticorrosion coatings for the benefit of molten salts TES applications.

MATERIALS AND METHODS: Metallic pieces of stainless and carbon steel were coated with nanoparticles of alumina and silica by different methods: sputtering, spray and slurry coating; to check their protective effectiveness. Corrosion tests and samples preparation for analysis after the experiments were conducted according to the protocols described elsewhere [4]. The samples of stainless/carbon steel were subjected to isothermal corrosion tests and characterized by SEM, EDX and XRD. Additionally, the mechanism responsible of this beneficial effect was investigated by means of nanoparticle diffusion experiments.

RESULTS: The application of nanoparticles-based coatings reduced the corrosion extent of the samples during the experiments. This modification was attributed to the inclusion of the nanoparticles in the surface of the metallic matrix during the corrosion process.

CONCLUSION: The coatings containing nanoparticles have shown their effectiveness for limiting the corrosivity of molten salts.

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HIGH TEMPERATURE EQUILIBRIA IN MOLTEN NITRATE SALT – THERMAL STABILITY IN PURGED AND CLOSED SYSTEMS

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INTRODUCTION: A mixture of sodium nitrate and potassium nitrate is a widely used material for sensible heat storage. At the present time, it faces an upper storage temperature limit of 565 °C, and the thermal stability is considered acceptable in large scale systems. Current developments strive for an increase of the maximum temperature for advanced power cycles, and to improve the storage efficiency [1]. However, thermally driven reactions intensify when the temperatures increase, and threaten to produce critical amounts of harmful decomposition products. The formation of oxide ions can be particularly problematic, because oxide ions relate to steel corrosion, and steel is used as construction material in storage systems. We present two approaches to stabilize molten salt at and above 600 °C. Either the gas atmosphere is purged with a defined mixture of stabilizing gases, or the system is closed to retain reaction gases. Both options provide system conditions that enable chemical equilibria, and in that way suppress salt decomposition.

MATERIALS AND METHODS: The experiments are executed in a custom-made test rig equipped with a purge gas system and automated sample extraction. About 100 g of salt are heated up to the target temperature (≥ 600 °C) followed by ~ 1000 h isotherms. For the first approach, the purge gas comprises nitrogen, argon, oxygen, and nitrogen monoxide. For the second approach, the system is sealed and the pressure in the gas phase is measured. The salt composition is analyzed by titration analysis and ion chromatography.

RESULTS: Mainly nitrate ions, nitrite ions, and oxide ions are found in the salt samples, all of them being reaction products of the nitrate ion decomposition process. The nitrite ion concentration mainly depends on the oxygen partial pressure, and a steady-state level of nitrite ions is observed as long as the oxygen partial pressure remains constant. The concentration of nitrite ions is lowered by increasing the oxygen partial pressure. The ratio of nitrate ions, nitrite ions and oxygen is described by a reaction equilibrium. Thermodynamic data is provided for several temperature ranges [2,3,4], and is comparable to the relevant literature [5,6]. A steady formation of oxide ions is found in experiments under nitrogen, synthetic air and argon-oxygen atmosphere. The two regarded approaches intend to prevent or retard the oxide formation process. Effectively, the content of oxide ions could be reduced by adding nitrogen monoxide to the gas purge. Part of the nitrogen monoxide reacts with oxygen to nitrogen dioxide. Hence, the observed stabilization effect is attributed to the nitrogen oxides (NO_x) as a whole. With increasing experiment temperature, the concentration of nitrogen oxides that is required to reduce the decomposition reactions also increases. For example, salt stabilization was achieved with 200 ppm NO_x at 600 °C, and with 500 ppm NO_x at 620 °C. [4] Similarly, closing the system distinctly reduces salt decomposition. The formation of both nitrite ions and oxide ions is inhibited. The measured pressure increase reveals the emergence of gases due to chemical reactions. Eventually, the pressure stabilizes, and the established partial pressures of the reaction gases induce chemical equilibria. [7]

CONCLUSIONS: The results of the stability investigations at and above 600 °C are interpreted with regard to the application of nitrate salts as heat storage material in TES systems. Steel corrosion is considered a major challenge at high temperatures, and the corrosion increases in the presence of oxide ions. The study reveals possibilities to suppress salt decomposition, and to maintain a low content of oxide ions. An adequate gas

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phase composition can be achieved by purging the system with a mixture of nitrogen, oxygen and nitrogen oxides. Salt stabilization is demonstrated at ambient pressure, and is therefore considered scalable. Closing the system showed equally stabilizing effects, and does not require additional gases for purging. The demonstrated options can be combined for large-scale energy storage systems to maintain thermal stability at prospectively high temperatures.

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HOT CORROSION RESISTANCE OF INCONEL 600 UNDER MOLTEN SALTS AT 675 °C FOR THERMAL ENERGY STORAGE TANKS

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INTRODUCTION: In 2018, according to data from the International Energy Agency (IEA) and the International Renewable Energy Agency (IRENA), of the total global energy production only 4.6% came from renewable energies and of this, only 8.3% was generated by solar energy.

Solar energy is a natural and infinite energy resource. It is extremely important to be able to capture it, store it and supply it to the distribution network without interruptions and adjusting to the demands.

To achieve this goal and for solar energy to form part of our lives in a greater percentage than today (0,38% of the global energy generation), it is necessary to overcome a series of challenges. The main one is to keep its supply constant to be able to cope with any energy demand during all hours of the day. Once the objective is achieved, it would be feasible to exceed the percentage of non-renewable energy sources.

To achieve a constant energy supply, it is necessary to improve current solar energy storage systems so that they are able to store enough energy to meet demand.

In this sense, various investigations have been carried out, both on the medium in which energy is stored (fluids, particulate solids, phase change materials, ...) and on the materials of the storage tank in concentrating solar power plants (CSPs)

Currently in CSPs, solar energy is stored by means of fluids, such as molten salts, mainly a non-eutectic binary salt mixture of sodium and potassium nitrate (60:40 wt%) known as "Solar salt". Its operating temperature range is between 390 to 565°C. Thanks to its low cost and relatively high heat capacity, it is a viable energy reserve for off-peak hours, thus achieving constant and uninterrupted operation.

Innovating in the improvement of thermal energy storage (TES) tanks is vital to strengthen the position of solar energy in the global energy landscape and make it grow. Currently one of the most advanced plants in solar thermal energy is Gemasolar in Fuentes de Andalucía, near Seville, Spain. It has TES molten salt storage tanks capable of generating a total clean electrical power of 80 GWh/year and 15 hours of power supply for the autonomous operation of the plant during off-peak hours.

For the viability of CSP plants it is necessary to achieve the maximum energy supply and the maximum hours of autonomy. Therefore, it is essential to investigate in molten salts that can store heat at higher temperatures while maintaining physical and chemical properties, and in the materials of TES tanks capable of increasing the service temperature of the CSP plant above the current 565°C.

MATERIALS AND METHODS: The research has been carried out on two eutectic mixtures of molten salts with working operating temperatures range between 630 to 850 °C.

Na₂CO₃ - NaCl (59,5:40,5 wt%, mixture 1) and Na₂SO₄ - NaCl (68,0:32,0 wt%, mixture 2). Both have been selected due to their low cost and excellent thermal properties (high operating temperature and high heat capacity). Nickel alloy, Inconel 600, has been selected for the tank due to its high resistance to corrosion at high temperatures although its cost is high (17,6 €/kg). Samples of (10x20x2 mm³) from a sheet have been used for tests.

The corrosion progress has been determined using EIS (Electrochemical Impedance Spectroscopy) and LPR (Linear Polarization Resistance) electrochemical techniques.

RESULTS: At 675 °C, for mixture 1, only 45 µm of corrosion layer is observed after 336 hours and 100 µm after 1800 hours, from an initial thickness of 2 mm. However, for mixture 2 it has been impossible to evaluate it beyond 336 hours (less than 14 days) due to the total delamination of Inconel 600.

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By EIS and LPR its observed for mixture 1 how the corrosion progresses constantly for 1800 hours. Nyquist plots show how capacitance decreases as the time progress. In addition, the Taffel curves show how the corrosion voltage cannot be maintained and oscillates between (-0.4 V and -0.1 V) during the entire analysis time.

CONCLUSION: The results obtained shown that there is no effective loss of mass or properties of Inconel 600 sheets in contact with mixture 1 at 675 °C after 1800 hours of exposure.

Corrosion voltage and capacitance values obtained from Taffel curves and Nyquist plots show that corrosion continues, and a fully protective layer is not formed under the operating conditions.

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CORROSION STUDY OF THE USE OF NITRATE MOLTEN SALT NANOFLUIDS IN CONCENTRATED SOLAR PLANTS

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INTRODUCTION: Concentrating solar power (CSP) systems allows to combine solar thermal power generation and large capacity thermal storage offering sustainable stable and adjustable high-quality power [1]. Molten salts in CSP systems can be used as heat transfer fluid and energy storage media [2][3], thus playing an important role in the overall performance of the CSP system. To increase the storage capacity and heat transfer in molten salts, nanofluids (base fluid with a small addition of particles < 100 nm) have been suggested as materials with higher specific heat capacity than the base fluid [4–6]. However, the compatibility of containment materials with the molten salt is a significant technical challenge for CSP plants [7] and it is necessary to understand and predict corrosiveness of molten salts when nanoparticles are added. Although corrosion of molten salts nanofluids has been studied, the scattered data found encourage further studies on these systems to support their application. In this study, the chemical compatibility between an industrial Solar Salt mixture (NaNO₃-KNO₃; 60:40 wt. %) with SiO₂ nanoparticles (0.5 wt. % and 1 wt. %) and four metals are studied: two stainless steel (304H and 316L), one carbon steel (AISI 1045) and one nickel alloy (Inconel 600). The authors are aimed to assess the effect of nanoparticles on the corrosion behaviour of the containment materials selected at 500 °C after 90 days of metal-salt contact.

MATERIALS AND METHODS: The binary molten salt composition formulated, 60 wt.% NaNO₃ and 40 wt.% KNO₃ was prepared through a static melting method, similar to that reported by Xie et al. [8]. The raw materials were dried at 100 °C for one hour, then mixed and heated up to the liquid phase. Then the molten salt with nanoparticles compositions, 0.5 wt.% and 1 wt.% of SiO₂, were prepared by a two-step method.

Based on the literature review, four metals were chosen: AISI 1045, 316L, 304H and Inconel 600. The corrosion test was performed under steady-state conditions at 500 °C, submerging the different metal samples in the Solar Salt inside alumina crucibles and removing the samples at 7, 15, 30, 60 and 90 days. Corrosion was studied by characterizing the oxides formed by scanning electronic microscope (SEM), Energy-dispersive X-ray spectrometer (EDS), and X-ray diffractometer. Two gravimetric methods (gravimetric weight method and descaled method) were used to determine the corrosion rates.

RESULTS: The corrosion rate values in micrometers/year at 90 days for the different metals with 0%, 0.5 % and 1 % of nanoparticle content are:

- AISI 1045 : 69.81; 272.36; 313.78
- 316L: 6.60; 3.93; 4.89
- 304H: 1.30; 6.46; 6.25
- Inconel 600: 0.29; 0.11; 0.67

The study shows that the increase in nanoparticles content, in general and in a different extent, lead to higher corrosion rates of the metals in contact with the different formulations. The metal that experiences the highest effect is the stainless steel 304H, followed by AISI 1045 and Inconel. 316L corrosion values seem to show a negative effect, but the error of the measurements does not lead to significant differences when compared to the base fluid. The corrosion resistance to molten salts of stainless steels is higher than the carbon steel, being 304H the highest. When adding nanoparticles, the corrosion resistance seems to be

higher in 316L (followed by 304H and AISI 1045). The standard deviation of the values obtained cannot reveal the effect of increasing the nanoparticles content. Besides, Inconel shows the lowest corrosion rate among all the metals.

CONCLUSIONS: The applicability of nanofluids in CSP plants was studied in terms of their effect on the corrosion resistance when the salts are in contact with the different metals in the system. The use of silica nanoparticles in the Solar Salt molten salt mixture led in general to an increase of the corrosion rate, which in some cases, like AISI 1045 carbon steel, the metal moves from being recommended to applications up to one year up to one-month length. For CSP applications, the lifetime of the system is expected to be more than 20 years [10], which makes a maximum recommended corrosion rate less than 0.02 mm/year. At high temperature, 500 °C just 304H, 316L and Inconel 600 can be used for long term service with nitrate-based nanofluids with up to 1 wt. % of SiO₂ nanoparticles.

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ANALYZING ONLINE NEWS TO UNDERSTAND THERMAL ENERGY STORAGE AWARENESS AND ACCEPTANCE

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INTRODUCTION: The global population is facing important socio-political, economic and environmental challenges, also due to the periodical crises happening all around the world, caused by a variety of natural and anthropogenic actions. People are exposed to different information concerning, for instance, climate change, global warming, and technological advances and their impact on society. This is particularly relevant for building occupants and designers when it regards thermal energy storage, as this represents a key evolution concerning any energy system and offering key benefits also from a building and industrial operation perspective. The Internet and the availability of online high quality data sources represent a true opportunity to make people aware of the new energy solutions and their advantages for environmental sustainability and energy saving. In this scenario, online news, social media platforms like Twitter, or search-volume data (such as Google Trends) become particularly relevant to study and create awareness about energy technologies and solutions. In this study, we focus on the analysis of online news data, which often make possible to understand and predict people's behavior, as well as plan actions to influence their future choices.

METHODOLOGY: In this study, we assess people's awareness of energy storage solutions and relate it to the message conveyed in online news. In order to do so, we firstly screened online news appeared on the most important online information service in the time period December 17, 2017 – December 23, 2018 selecting those referring to energy topics. At a second stage we assessed the semantic importance of Energy-Storage-Terms (ESTs), combining methods and tools of text mining and social network analysis, i.e. using an index known as the Semantic Brand Score (SBS). The SBS is made of three dimensions: (i) prevalence, (ii) diversity, and (iii) connectivity. Prevalence identifies the frequency of appearance of ESTs in a discourse and evaluates their visibility. Diversity measures the heterogeneity and uniqueness of the words that are frequently co-mentioned with ESTs. It can be considered as the richness of context and information related to a brand or topic. Connectivity expresses the brokerage power of ESTs, i.e. their ability to link different discourse topics. Combining these three dimensions leads to the measure of semantic importance, i.e. the SBS. We used the SBS theoretical framework to investigate societal awareness about ESTs – with a specific focus on thermal energy storage. In doing so we were able to identify the key drivers in thermal energy storage communication patterns, as well as their most important relationship with other energy-related topics. As a final step, we identified the most promising communications strategies that should be followed for better exploiting and fostering thermal energy storage solutions and technologies, particularly, in the building sector.

RESULTS: Results show the importance trends of ERTs in online news and additionally analyze their textual associations. Focusing on energy storage, we find that this topic would benefit from a stronger association to the topics of energy efficiency, green energy and renewables. Leveraging the visibility of these themes could improve its importance and facilitate the implementation of its technology on a broader basis.

CONCLUSIONS: The SBS approach shows to be applicable in a variety of energy and environmental contexts, potentially with the aim of supporting the diffusion of new standards, policies and energy saving practices.

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The same methodology could also be applied to identify information gaps, which may be reduced through improved media coverage.

ANALYSIS OF ELECTRICITY CONSUMPTION IN SLOVENIA UNTIL 2050 BY INTEGRATING RES WITH THE ROLE OF ENERGY STORAGE TECHNOLOGIES

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INTRODUCTION: One of the main objectives of energy policy in the European Union (EU) is to gradually increase the use of renewable energy sources (RES) and improve energy efficiency. The main reason for this is the need to reduce energy consumption, environmental impact and dependence on fossil fuels. The EU aims to be climate-neutral and free of greenhouse gas emissions by 2050. In order to achieve this, Slovenia should pursue its targets and in this context achieve a share of at least 27% RES of gross final energy consumption and 43% of RES electricity generation by 2030.

MATERIALS AND METHODS: The main objective of this study is to provide a scenario-based assessment of the development of energy consumption, focusing on the projection of electricity consumption up to 2050 for the Slovenian electricity transmission system. The main objective is to determine the demand for electricity in the transmission network and the load on the transmission system for domestic consumption. One of the main challenges is how to properly integrate energy storage technologies for balancing the complex nature of energy consumption on the one hand and the challenges of RES integration for energy production on the other. The scenarios analysed for electricity consumption are based on the established MEDEE methodology followed by ENTSO-E guidelines.

RESULTS AND CONCLUSIONS: The results within the different scenarios show that we need an appropriate integration of energy storage technologies into the future Slovenian energy network (Smart Grid) in order to achieve the ambitious EU target for 2050.

A TECHNO-ECONOMIC ANALYSIS OF COMPACT THERMAL ENERGY STORAGE TECHNOLOGY: ENERGY & COST SAVINGS, LOAD-SHIFTING POTENTIAL, AND 2030 COST TARGETS

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INTRODUCTION: Techno-economic analysis is a critical first step to evaluating the attributes of novel residential thermal energy storage (RTES) technologies and identifying suitable market entry points for deployment. In this study, a custom spreadsheet tool was used to obtain a high-level outlook of the hourly performance of various RTES technologies for four different housing archetypes in thirteen representative cities of provinces and territories across Canada. Three integration scenarios are considered, including a compact thermal energy storage (CTES) module filled with thermochemical sorption material in combination with: i) electric resistance heaters; ii) an air-source heat pump; and, iii) a solar combi system.

METHODS AND MATERIALS: Energy models of each CTES scenario were developed as a balance of plant to meet the heating load for a given home archetype in a set region. Hourly weather and heating load data for a given city and typical meteorological year (TMY) were used to determine the required thermal performance of each modeled technology system integration scenario. Forecasted time of use rates and schedules for utilities controlled the operation of the RTES systems. Additionally, capital equipment costs and operational expenditures determined the net present value of each technology over a defined lifetime. Two control strategies for the charge and discharge of the CTES were considered: i) time-of-use and charging during “off-peak” hours and discharging during “on-peak” hours; and, ii) concurrent charging and discharging to maintain a flat electrical demand for heating.

RESULTS: For the selected CTES integrated system designs and target storage density considered, the energy & cost savings, load shifting capabilities, and target installation cost of CTES technology were determined for each scenario. Overall, the results of the simulations presented in this paper show that CTES technology could promise significant energy and utility bill savings by shifting loads from high-demand to low-demand periods. The configuration of a 1 m³ CTES system installed alongside an air-source heat pump was determined to provide competitive cost savings for older homes in Atlantic Canada and the province of Quebec when compared to standalone heat pump systems. Furthermore, the performance of a CTES-heat pump system is considered for an electrified heating scenario during the coldest 24 hours, days, and weeks with “extreme meteorological year” weather files extracted from multi-year data (EMYs). Additional sensitivity analyses show the effect of control strategies and CTES module size on lowering and flattening the electrical demand for heating.

CONCLUSION: Provided that the assumed CTES performance and cost target are met, the estimated load shifting capabilities demonstrated by CTES technology indicate that it could lend itself well to supporting the electrification of the Canadian residential heating load. CTES systems in select regions were determined to provide positive net present value and that it is competitive with conventional electric-resistance and oil & gas-based heating systems. Lower and more uniform electrical demand peaks can be realized through control strategies that allow simultaneous charging and discharging of the CTES on the coldest days of the year.

THE INFLUENCE OF DISTINCTIVE URBAN MORPHOLOGIES ON THE MICROCLIMATE IN SINGAPORE

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INTRODUCTION: The global urban population is projected to grow by 2.5 billion urban dwellers between 2018 and 2050, with nearly 90 per cent of the increase concentrated in Asia and Africa. Increasing evidence for the impact of climate change and the effects of natural hazards on populated areas emphasize the need for better planned and re-imagined cities. High-density cities such as Singapore have to deal with the urban heat island (UHI) effect, which is one of the most critical anthropogenic environmental issues for contemporary high-density cities. As cities grow denser and hotter, a climate-responsive landscape planning can create a more liveable urban microclimate with adequate human comfort. In this context, the study aims to investigate the effects of different urban morphologies such as high-rise and low-rise buildings, green areas, and water bodies on urban microclimate in Singapore.

MATERIALS AND METHODS: Mobile surveys were conducted to explore the severity of the UHI effect through distinctive urban morphologies. The Sky View Factor (SVF) was also calculated. The walking paths were performed in the city center of Singapore, starting at the City Park and finishing at the Promontory (Marina Bay Waterfront Boulevard). The path was chosen to encompass a park (green area), low-rise buildings, high-rise buildings, and water area. Mobile traverses were conducted during February 2020. Survey times were afternoon (15.30h – 16.15h), evening (19.00h-20.00h) and midnight (01.00h-01.40h). All measurements were carried out during clear and windless days in open areas. Avoidance of windy and cloudy conditions minimized the influence of meteorological variables.

RESULTS: This study revealed a strong correlation between the decrease in the air temperature and the appearance of green areas in the city. Moreover, during daytime, it was found out that the higher the SVF, the higher the air temperature.

CONCLUSIONS: Parks or clusters of trees are able to provide shading during daytime and evaporative cooling at nighttime. Thus, the air temperature throughout the day can be maintained at a relatively cool level. However, although the transpiration of green areas can reduce air temperature, shading is a much more important factor in tropical cities. Therefore, it can be concluded that during daytime, shading is the most important factor in providing a cooler air temperature and comfort, especially in tropical climates.

ROLE OF ONSITE THERMAL AND ELECTRIC STORAGE IN NZEBs

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At the end of 2020, all new buildings in the European Union (EU) must be nearly zero-energy buildings (nZEBs) in order to contribute to the achievement of the EU-CO₂ neutrality by 2050. As the technical options to achieve highly-efficient building envelopes are available and well-known, there is no doubt that the most promising HVAC systems will include heat pumps (HPs) and photovoltaic (PV) panels. However, there exist ongoing discussions on the optimal system layout and the integration of storage to achieve nZEB. In particular, there are some good arguments in favour of very low demand, while contrariwise also high flexibility is seen as an important feature to enable so-called grid-reactive operation of the building stock.

According to EPBD, an nZEB is a nearly zero- energy building, meaning that such a building has a very low energy demand due to efficiency measures that include efficient HVAC technology and utilization of renewables. Yet, in the EU member states nZEBs are defined following some national standards. In this regard, each member state provides its own national definition with significant differences in terms of energy consumption (heating, cooling, hot water, auxiliary consumers and appliances), maximum limits, conversion factors, etc. (see BPIE, 2016).

In this paper a method to compare the so-called ambition level (i.e. the comparison of the deviation in terms of lifecycle costs and primary energy requirements for the cost-optimal option) considering different climatic and boundary conditions is presented. For this purpose, an exemplary case study of an individual single-family-house with air-water heat pump and storage is studied using simulation tools. Various heat pump concepts for the realization of nZEBs were investigated. Herein, the investigation included the heat pump integration together with locally available renewable energy sources for application in nZEBs. In this context, a special focus was on the optimization of the heat pump control. Further, the monitoring results of different heat pumps were analysed for a selected number of projects.

For all virtual case studies primary energy savings and the capitalized total annual costs are evaluated. A techno-economic analysis of different technologies including passive components (envelope, MHVR, SDWR), active components (heat pump), renewables (ST, PV, PVT) as well as storage is performed: cost-optimal solutions and combinations can be identified depending on the climate and type of building (i.e. residential and non-residential buildings) as well as on the application (heating, cooling, DHW, lighting, appliances). The cost efficiency of different technologies is evaluated vs. their primary energy savings. Special focus will be given on the integration of onsite storage and its influence on the energy demand of the buildings and the peak power was investigated.

The aim is to show for the investigated virtual cases the potential of integrating passive and active solar technology and the role of onsite storage. A methodology was developed to analyse and compare different solutions. Based on the presented results design guidelines can be elaborated. Furthermore, the results can be used to further foster and optimize nZEB design and implementation and the role of storage.

EFFECT OF THE PROCESSING METHOD IN TRIMETHYLOLETHANE BASED COMPOSITES FOR THERMAL ENERGY STORAGE SYSTEMS

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INTRODUCTION: Trimethylolethane (TME) belongs to the family of materials known as Plastic Crystals, which are an attractive option for thermal energy storage (TES) systems on account of their energetic solid-solid phase transition. Subcooling, low thermal conductivity, reliability or poor mechanical resistance at high temperature are obstacles that must be overcome to bring these materials closer to real applications. The use of Expanded Graphite (EG) as additive is a promising alternative to address these challenges. Although some works have been done in this sense, to date, no focus has been placed on the processing methods of these composites despite the great effect they have on the final properties of the material. From a practical point of view, this work examines the effect of two processing methods (cold pressing and melt processing) on the final properties of TME/EG composites. These two processing methods lead to quite different microstructures which, undoubtedly, generate different performances. Thermal properties of TME/EG composites such as latent heat, thermal conductivity and subcooling, as well as the obtained shape-stability and their relationship with microstructure are studied in this work.

MATERIALS AND METHODS: Samples having different EG weight content as well as two different EG particle sizes were obtained by means of both pressing and melt processing techniques. The thermal properties of the obtained composites were analyzed by DSC and hot disk, whereas helium pycnometer and SEM were used to study their microstructure.

RESULTS AND CONCLUSIONS: the use of melt processing promotes higher porosities than pressing due to the formation of dendrites during solidification. In addition, the distribution of EG within TME is strongly affected by the processing method. These changes in the microstructure result in different thermal properties. Melt processing induces a drop in the latent heat of the samples, which, in addition, is more pronounced as the EG content increases in melt processing samples. Therefore, pressing leads to composites with higher thermal conductivities, lower subcooling and greater latent heats than the exhibited by the samples obtained by melt processing.

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PARAMETRIC CHARACTERIZATION OF THE VARIABLES THAT INFLUENCE SUPERCOOLING ON PCMS

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INTRODUCTION: Thermal energy storage (TES) has become increasingly important in engineering applications that involve intermittent energy sources, such as most renewables. Latent heat thermal energy storage (LHTES) relies on the use of Phase Change Materials (PCMs), which store thermal energy by the latent heat required for the melting/solidification process.

Amongst other requirements, materials used as PCMs normally have to show a reduced supercooling [1]. According to the literature [2], the following parameters influence the supercooling degree: volume/mass (related to the homogeneous nucleation theory); the existence of crystals or solidary surfaces (related to the heterogeneous nucleation theory), and the cooling rate. However, discrepancies can still be found in the literature regarding the parameters that affect the supercooling behavior.

In large-scale storage applications, nucleation is normally associated with the fact that the sample volume is large enough to include some exogenous nuclei. This stochastic effect could explain the typically unpredictable supercooling reported in PCMs. However, other factors such as a system heterogeneous temperature distribution could also explain the claimed unpredictability, which is highly dependent on the system geometry and the external cooling conditions. Besides, different PCMs may have a different nucleation response because of their different characteristics. Studies regarding the influence of variables such as mass or cooling rate can be found in the literature; however, to our best knowledge, no article deals with the interaction between the set of different potential influencing parameters.

As a result, an experimental study is herein performed, in order to assess the influence of several process-related parameters on the crystallization temperature of two PCMs. It is intended to gain knowledge about their effect on the supercooling degree and to develop simplified correlations that help to predict the supercooling behavior of the involved materials.

MATERIALS AND METHODS: The study comprised five different container configurations, two heating/cooling media, several different cooling rates, and two different PCMs: urea and sodium nitrate eutectic mixture and polyethylene glycol 10000. They were selected due to their melting temperature, suitable for heating and domestic hot water applications. The urea and sodium nitrate eutectic mixture was previously identified as a PCM candidate by the authors [3]. It presents a melting point of 85 °C and a fusion enthalpy of 172 J/g. Previous DSC tests revealed a supercooling degree between 24 and 48 °C. Polyethylene glycol 10000 melts at 58 °C and has a latent enthalpy of 175 J/g (both experimentally determined by DSC). According to the literature [4], it exhibits a supercooling degree up to 20 °C.

The experiments consisted of heating up the PCM samples above their melting temperature to ensure a full melting. They were then cooled-down upon different experimental conditions to undergo different cooling rates under various heat transfer coefficients. The PCM samples were monitored from the melt to determine their behavior upon solidification.

RESULTS AND CONCLUSIONS: The testing conditions produced different supercooling degrees for each PCM and testing conditions. A new characterization approach was set from a practical and technical point of view. It consisted of the analysis of the supercooling degree as a function of the following 7 variables:

sample mass (m); a characteristic length (L_c), defined as the volume/surface ratio and representative of the geometry; cooling rate (v_{HTF}) of the heat transfer fluid (HTF); cooling rate (v_{PCM}) of the PCM; heat transfer coefficient (h), which described the external cooling flow behaviour and, finally, the PCM thermal conductivity (k) and thermal diffusivity (α).

A statistical analysis of the results was performed by the R-Commander software, so as to establish the parameters that are more relevant for the crystallization process. A correlation test was first performed, using Pearson's correlation coefficient as a measure of their individual relevance on the crystallization temperature. The relevance of their association (multiplication and division of the variables) was studied as well.

Results gave evidence for the ratio between the HTF cooling rate and the container characteristic length (v_{HTF}/L_c) to be the most relevant parameter in the supercooling degree, with a Pearson correlation coefficient of 0.97. These variables, v_{HTF} and L_c , can be controlled or acted on in a direct way. This finding highlights the importance of the geometry or mass disposition regarding the supercooling degree rather than the direct effect of the mass itself.

The second most relevant parameter was the PCM cooling rate (v_{PCM}), followed by, the heat transfer coefficient (h) of the surrounding medium. The former variable has been usually reported as an influencing parameter for supercooling; however, the contribution of the heat transfer coefficient has been traditionally omitted. The rest of the studied variables showed a reduced influence on the supercooling effect, at least in the studied conditions.

In addition, linear regression models to describe the supercooling degree of each studied PCM in function of the most relevant variables were determined. The best-fitting models for both materials include v_{HTF}/L_c and h , with an R-squared value of 0.95 for the case of urea and sodium nitrate eutectic mixture, and 0.94 for polyethylene glycol 10000.

From the performed data analysis it was not possible to establish an accurate correlation that might be used for the two selected materials; however, the methodology was able to assess the variables that can be used with this aim. Further research should be pointed towards this limitation, in order to achieve a relationship that can be valid for different PCMs and various crystallization temperature ranges.

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THERMAL CHARACTERISATION OF THE NOVEL Cu-67 WT. % Mg PHASE CHANGE MATERIAL FOR THERMAL STORAGE APPLICATIONS

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INTRODUCTION: Nowadays metals and metal alloys are among the most promising phase change materials (PCMs) due to their high-energy storage density and high thermal conductivity relative to common molten salts and organic thermal storage materials. Metallic phase change materials are also attractive as they have a suitable melting temperature for thermal energy storage (TES) applications. The thermal storage group at the Institute of Material Physics in Space at the German Aerospace Centre is focused on metallic PCMs as well as their potential container materials. The binary eutectic composition Cu-67 wt. % Mg has been chosen as a new latent heat storage material suitable for space heating in electric vehicles, due to its melting point of approximately 487 °C and potential compatibility with iron. This presentation covers the characterisation of thermophysical properties including melting temperature, heat of fusion, heat capacity and thermal conductivity. The experimental procedure will be presented, describing the melting behaviour in metallic PCMs as well as recommendations for experimenting on Mg containing alloys.

MATERIALS AND METHODS: Differential Scanning Calorimetry (DSC) was used to determine the melting temperature, heat of fusion and heat capacity of the Cu-67 wt. % Mg alloy. Samples of approximately 20 mg were placed in Pt-Rh crucibles with alumina liners and perforated lids. Two heating and cooling cycles were performed with a heating rate of 10 K/min in a Netzsch 404 C Pegasus®. Larger samples were analysed using the light flash apparatus, Netzsch LFA 467 HT HyperFlash® to determine the thermal diffusivity in the solid and liquid states. Four cylindrical samples of approximately 750 mg were analysed under a flow of 5.0 argon gas from room temperature to 525 °C with 5 measurements at each 25 °C step.

RESULTS: Overall, the DSC results show that the Cu-67 wt. % Mg has a single endothermic transition indicating a eutectic temperature of 492 °C, which is in good agreement with the phase diagram. The solidification curves confirm the eutectic composition of the alloy. Latent heat of fusion value is 213 kJ/kg. Thermal diffusivity and calculated thermal conductivity in the solid state average 60 mm²/s and 130 W/m K respectively. In the liquid state 25 mm²/s and 50 W/mK were measured. The thermal transport properties are excellent when compared to other alloys and orders of magnitude higher than salts or organic phase change materials.

CONCLUSION: In this work, a novel Cu-67 wt. % Mg alloy has been proposed due to the great potential as a thermal storage material. Thermophysical properties were experimentally determined demonstrating an appropriate melting temperature and suitable heat of fusion for application as a mPCM. The thermal conductivity and diffusivity were also measured and found to be exceptional.

TESTING THE USE OF UA-VALUES FOR COMPARISON OF TWO DIFFERENT PCM-HEAT EXCHANGER

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A major issue with phase change material (PCM) heat exchanger (HX) is the current lack of design guidelines linking the PCM-HX to be built to the application requirements it needs to satisfy (heat transfer rates, total energy storage, etc). Before getting to design rules, engineers must first have a proper way to compare various designs in terms of their performance. One possible avenue for comparison being discussed at the moment is the use of a UA-value to characterize a given PCM-HX working under a given set of operating parameters. This UA-value then offers the potential to be used as a comparative metric between PCM-HX.

The results presented in this article will go back to two experimental studies performed at the authors' Lab of Applied Multiphase Thermal Engineering (LAMTE) looking at heat transfer rates in PCM-HX: a finned-tube system with varying number of tubes (4, 8 and 12) and a coil-and-tank system with varying numbers of coils (1, 2 and 3). The results from both studies will now be reframed and analyzed in terms of the UA-value obtained from each experiment.

In light of the results, the appropriateness of defining and using a UA-value to compare different PCM-HX will be discussed.

This work falls along a series of analysis and discussion in the latent heat storage community to explore and determine the best way forward to compare, and eventually, determine design rules for PCM-HX.

PARAMETRIC STUDY OF THE PCM SYSTEM FOR SPACE COOLING IMPROVED WITH THE NIGHT-TIME VENTILATION FOR THE ENHANCED SOLIDIFICATION

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INTRODUCTION: Thermally well-insulated lightweight framed buildings prevent heat losses through their envelope and reduce the energy demand over the heating season. However, the heat capacity of the lightweight wall is relatively low and in summer, the building lacks thermal stability and overheats. Phase change materials (PCM) are broadly investigated for their well-known benefits of improving the indoor thermal comfort by decreasing the indoor temperatures while reducing the energy needed for space cooling when melting. However, when selecting the product, the important factors to consider are the optimal melting temperature (MT) and the amount of the material required. Moreover, due to low material density (insulation effect) and high indoor temperatures at night, the material does not completely solidify over the night cycle and does not fully perform in the day cycle. For the purpose of improving the PCM's performance, the air gap between the wall and the PCM is established, which is then ventilated with an outdoor air over the night time cycle.

METHOD: The validated model is established with 19.1 ANSYS Fluent™ software. The evaluation is performed in an office room with one window oriented to the south. The thermal comfort aims to be improved by the addition of macro-encapsulated PCM plates to the wall opposing to the window and to the ceiling. The wall-ceiling PCM plates with the original wall form an air gap. During the day cycle, the PCM material plates are melted by solar radiation and internal gains. During the night time, the air gap is ventilated with the outdoor air ($T_{avg} = 18.1$ °C). In order to investigate the performance of such system, the parametrical study is obtained based on the geometry of the inlet air diffuser, inlet air temperature, airflow rate in the air gap and the MT (21 °C, 22 °C, 24 °C and 25 °C) of the PCM plates. The system's performance is accessed based on the solidification time and the energy needed for the solidification of the system.

RESULTS: The results show that the highest flow and the lowest inlet air temperature solidify the plates in the shortest time. However, the energy needed to provide large amounts of air is consequently the highest.

CONCLUSION: The existing lightweight non-residential office buildings are equipped with a ventilation system for improving the indoor air quality in the day time, but unused during the night time. Thus, such a PCM system has a large renovation potential, since the ventilation is already present in the office and it doesn't require large modifications. The electrical energy tariff at the nighttime is lower compared to the daytime. Additionally, in the nighttime, the large cities with a considerable amount of non-residential office buildings are often obliged to sell their surplus of electrical energy abroad. Such electricity may be used for actively discharging the PCM systems, which are in the day time passively charged.

PROMOTION OF THERMAL COMFORT THANKS TO PCM: ALSO STILL AFTER 10 YEARS OF OPERATION?

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INTRODUCTION: Intensive research and development on latent heat storages (PCM) in buildings has been done since more than two decades in order to face increasing overheating issues without rising usage of cooling energy demand. During the ongoing project PCM Eval experiences on the long term functionality as well as the users' valuation and satisfaction in respect of system functionality were collected. The real performance of a PCM system, especially in passive cooling concepts using night ventilation for regeneration, is strongly depending on the building users' behaviour. Often contrary decisions need to be made by the user e.g. between an increased air quality and hence increased heat input when a window is opened during daytime in summer. In many cases user behaviour is not sufficiently taken into account during the design phase, leading to an insufficient usage of the PCM systems.

MATERIALS & METHODS: This work presents results of the case study in Straelen/Germany, which is a city hall building partially equipped with PCM containing plasterboards. To determine the indoor climate and the benefit through PCM after ten years of operation, one office room of the building was monitored for several weeks. Based on this data, a building model was created with EnergyPlus and various scenarios were simulated to analyze the influence of the PCM and user behavior (window ventilation, use of blinds) on thermal comfort.

RESULTS & CONCLUSION: Measured data showed, that after ten years of operation the PCM still had a smoothing effect on temperature, but the average temperature decrease of 0.6 K through PCM was quite lower than expected from literature. Nevertheless, cooling degree hours (CDH) were reduced by 31% through PCM during the summer period, which represented a significant comfort improvement. Further simulation results indicate that the users' behavior (window ventilation, shading) can have a great influence on thermal comfort and can better exploit the previously unused PCM potential if they adapt their behavior.

THERMAL ANALYSIS AND SIMULATION OF SOLAR BUILDING HEATING SYSTEMS UTILIZING HEAT PUMPS AND PHASE CHANGE ENERGY STORAGE

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Practical and design difficulties always arise when a designer tries to provide a significant solar contribution to meeting the heating loads of a building. Solar resource is low during the months of the heating season, being difficult to collect large amounts of solar energy. Additionally, the marked energy mismatch given between solar energy and heating demand curves on a daily basis, makes necessary the use of thermal energy storage systems to increase (up to a significant fraction) the solar contribution to the heating load, storing solar energy from midday hours when solar radiation is high to late afternoon or night when the building heating demand peaks.

Although large solar collector areas and storage capacities combined with low-temperature terminal heating units (typically radiant floors) are common features of the few solar building heating systems currently in operation, still they are only able to achieve relatively low yearly solar fractions (in the range of 20-40%). To increase the solar contribution to the building heating demand, this study considers the inclusion of two additional components into the solar active system: a phase change energy storage tank, integrated into the collector loop to store a greater amount of solar energy (although at a lower temperature level); and a water-to-water heat pump operating between this phase change storage tank (heat source at a low temperature level) and building's radiant floor (heat sink at the high temperature level).

The proposed system exhibits two clear advantages from an energy source and efficiency standpoints: from an energy source point of view, this system only consumes electricity (in the circulating pumps and the heat pump), not requiring the intervention of any fuel-burning equipment, which will become harder to install, or even banned by the increasingly stricter energy codes in the forthcoming years (e.g., 2050 in Europe). From an energy efficiency point of view, both additional elements will operate efficiently, as they are subjected to very favourable conditions: the phase change storage tank will reduce the average temperature of solar collectors (the selected PCM melting point is around 27 °C), increasing their collection efficiency. Additionally, during heat pump operation, the source and sink temperature levels are maintained within a small (only around 10-15 °C) and stable range because of the phase change, enabling the heat pump to operate with a higher COP (lower electric consumption) and greater heating capacity.

To predict its energy performance, the proposed system has been modelled in TRNSYS 18, including as a non-standard component, a storage tank containing macro-encapsulated phase change materials in the collector loop. This tank model was experimentally calibrated in a previous work, being compiled into the TRNSYS component Type 3260, to accurately assess the impact of integrating a phase change storage tank into a HVAC system. A two-floor single-family house with the building geometry of the single-family house used in IEA SHC-TASK 32 and located at Madrid (Spain) was considered in the TRNSYS simulations. Building envelope characteristics were selected to meet new building Spanish codes for the weather conditions of Madrid.

TECHNO-ECONOMIC EVALUATION OF NITRATE SALT STORAGE CONCEPTS AT 620 °C

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INTRODUCTION: The production of dispatchable electricity from volatile renewable energy such as wind and PV requires energy storage. Retrofitting existing fossil fired power plants with thermal energy storage, and ultimately transferring them to heat storage plants, is a promising and low-cost option for implementing large amounts of grid scale energy storage [1]. State of the art molten salt thermal energy storage is used up to a maximum temperature of 565 °C, while modern supercritical steam power plants operate at temperatures above 600 °C for optimum efficiency. Previous work has shown that the thermal stability of molten nitrate salt can be improved by providing specially composed gas phases [2,3]. Therefore, the design of the gas system is decisive for the new generation of nitrate storage systems up to 620°C. This study presents a techno-economical comparison of conceptual designs including gas systems for large-scale molten salt thermal energy storage with operation temperatures of 620 °C. The interaction between the technological demand for high temperatures, requirements for material stability and the economic perspective are evaluated.

MATERIALS AND METHODS: The proposed storage concepts with nitrate salts at elevated temperatures all require a gas handling system to prevent salt degradation. In a first step, different gas handling systems are optimally designed based on net present value method. Examples are closed systems with active tank pressure control and half-open system with purge gas control. Previous work indicates that the formation of corrosive impurities (e.g. oxide ion) may be significantly reduced by a controlled gas atmosphere, but structural materials for 620 °C have not yet been identified. In order to evaluate the potential of the approach, we use a simplified assumption that similar structural material as for the 565 °C can be utilized. In a second step, the different storage technologies (two-tank and single tank) are assessed in combination with a supercritical power cycle. The cost of dispatchable power is used as a measure to compare the proposed storage concepts at 620 °C with state of the art molten salt two tank storage at 565 °C.

RESULTS: The techno-economic analysis of the gas handling system reveals an optimum for temperature and pressure in the case of a closed system with active tank pressure control. Furthermore, it is shown, that the cost of dispatchable power generation from a supercritical power plant with 620 °C nitrate salt storage can be lower compared to a subcritical power plant with state of the art 565 °C nitrate salt storage, depending on the cost of the charging power.

CONCLUSION: Installing a gas handling system for nitrate salt thermal energy storage can increase the maximum temperature from 565 °C to 620 °C, ultimately increasing the amount of energy that can be stored per unit volume. Moreover, the full potential of the high efficiency of a supercritical steam power cycle can be exploited by implementing 620 °C nitrate salt storage. The additional investment for the 620 °C storage system is compared to the benefits of a higher power block efficiency and potentially lower storage costs using the cost of dispatchable power generation.

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ENERSTOCK 2021

Oral lectures

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EXPERIMENTAL COMPARISON OF SMALL-SCALE AND FULL-SCALE LATENT STORAGE FOR INTEGRATION IN EFFICIENT HEAT PUMPS

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Electrification of the energy system at small-scale and district-scale is becoming a reality, thanks to the development of solutions to increase the penetration of renewables, especially variable renewables, within the grid. The integration of heat pumps with storage systems allows the conversion of excess electricity during hours where there is an excess of electricity production or the cost of energy is lower, for its subsequent application when there is a peak in the demand from the load. The positive effect is not only on the grid, for the load levelling and the possibility of exploiting more renewable energy, but also for the end users who experience economic benefits.

In this context, a latent storage system was developed, for the integration inside a vapour compression cycle. It is based on a high-density finned heat exchanger, and includes both the passages for the refrigerant and for the Heat Transfer Fluid (water), thus working as a three-fluids heat exchanger (HEX) (Refrigerant-PCM-Water, RPW-HEX). The storage medium is a commercial paraffin with nominal melting temperature of 4°C, which was embedded between the fins of the HEX.

In order to have optimal heat transfer, the channels are distributed regularly, according to the following pattern: refrigerant – PCM – HTF, with the refrigerant and HTF fluids in counter-flow configuration. Two different storages were tested, small-scale and large-scale, characterized by the same geometric characteristics of the fins used and the position of the manifolds for the distribution of the HTF circuit, which are placed on the opposite sides of the HEX. The fins used in the PCM channels are dense enough to allow good contact with the PCM and high enough to hold as much PCM as possible. The high-density and strong structure also guarantee mechanical stability to withstand stresses from density changes resulting from the phase change of the PCM.

The small-scale system was tested in a dedicated setup at University of Lleida, whereas the full-scale one was tested already integrated in a commercial heat pump at CNR ITAE. The results were compared in terms of storage density, average power for charge and discharge and time needed to complete the process.

The results were critically discussed to identify possible rules for scale-up, as well as critical issues when sizing a full-scale storage.

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SHORT ORAL PRESENTATIONS - POSTER

ASTEP PROJECT: DEVELOPMENT OF HIGH TEMPERATURE THERMAL ENERGY STORAGE SYSTEMS FOR INDUSTRIAL PROCESSES.

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INTRODUCTION: Application of Solar Thermal Energy to Processes (ASTEP) will create a new innovative Solar Heating for Industrial Processes (SHIP) concept focused on overcoming the current limitations of these systems. This solution is based on modular and flexible integration of two innovative designs for the solar collector (SunDial) and the Thermal Energy Storage (TES, based on Phase Change Materials, PCM) integrated via a control system which will allow flexible operation to maintain continuous service against the unpredictable nature of the solar source and partially during night operation. ASTEP will demonstrate its capability to cover a substantial part of the heat demand of the process industry at temperatures above 150 °C and for latitudes where current designs are not able to supply it. Its modularity and compactness will also enable easy installation and repair with reduced space requirements, while most of components can be sourced locally. The ASTEP's process integration will allow full compatibility with the existing systems of potential end-users of SHIP. These aspects will provide a very competitive solution to substitute fossil fuel consumption. The developed solar concept will be tested at two industrial sites to prove the objective's target of TRL5. Life Cycle Analysis will be included to validate and demonstrate the efficiency of the proposed technologies. The first Industrial Site of the proposal is the world's leading steel company, ArcelorMittal, with a heating demand above 220 °C for a factory located at a latitude of 47.1 N (Iasi, Romania). The second site is the dairy company MANDREKAS, located at a latitude of 37.93 N (Corinth, Greece) with a heating demand for steam at 175 °C and a cooling demand at 5 °C. These test locations will validate the ASTEP solution for a substantial part of the potential requirements of industrial heating and cooling demand of the European Union (EU28), which is estimated at approximately 72 TWh per year.

MATERIALS AND METHODS: This ASTEP project requires the design of a hybrid Thermal Energy Storage (TES) system, considering three subsystems:

a) PCM selected for two end-user's requirements; b) shell-side inserts; and c) active hydraulic circuit and regulation. The selection of an optimal geometry for the inserts and multi-tube system, by means of modelling and simulation of the unsteady heat transfer phenomena during charging and discharging of heat energy in the storage system will be critical for the correct design of the system. Additionally, this objective will require a selection of metal alloy-based materials for the inserts and assess investment casting and assembly procedures.

RESULTS: A hybrid thermal energy storage system, consisting of the combination of passive and active heat transfer enhancement techniques, is to be developed with the aim of accumulating the excess of solar thermal energy during peak production hours, and to deliver it through the end user's demand under controlled power conditions.

It is planned to design and execute two energy storage units: one will be based on PCM characterized by a lower melting point, above 150 °C, and for this unit rather multi-component mixture of salts is preferred as a PCM material. Selection of molar ratio of mixtures allows to tailor its melting range, which at eutectic

ENERSTOCK 2021

Short oral lectures/posters

composition reaches minimal value. The second PCM is foreseen for higher working temperatures above 230 °C and can be based on single or multi component PCM.

CONCLUSIONS: Most current scientific and technological reports describing future scenarios of the European energy landscape agree that energy storage will be the one of the main tools to support the energy transition. The application of phase change materials (PCM) for solar thermal energy storage is a promising technology for solving the time delay between thermal energy production and consumption. Importantly, latent PCM has multiple times storage capacity compared to sensible heat materials, ranging from 50 to 150 kWh/t with efficiency between 75 and 90%.

Despite these advantages, the integration of latent thermal energy storage (LTES) systems in solar thermal facilities still lacks some technological features that prevent their technical and economic feasibility: typical heat transfer configurations for high temperature latent thermal energy storage comprise the use of shell and tube arrangements, owing to its robust construction geometry. Conversely, the limited surface-to-volume ratio yields very low charging and discharging velocities, which results in low heat transfer effectiveness of this type of LTES design. Additionally, this configuration does not allow the separation of capacity and power.

As pointed out by EASE EERA, the development of active heat exchange systems with a controllable heat transfer power is of paramount importance for the broad implementation in the market of the LTES technology.

The use of honeycomb inserts, as energy storage concept for this proposal, is intended for increasing the surface-to-volume ratio in the storage system. At the same time, the mechanical integrity of the honeycomb, compared to other inserts like metallic foams, will ensure the null impact of the thermal cycling on the long-term effectiveness of the system.

The hybrid nature of the thermal storage system to be implemented accounts for an active control of the power release, based on the regulation of the mass flow distribution across the multi-tube arrangement. This is of special interest for designing a LTES system with separated thermal capacity and power.

GROUNDWATER INFLUENCE ON LARGE-SCALE HOT WATER TANKS AND PITS FOR RENEWABLES-BASED DISTRICT HEATING SYSTEMS: TECHNICAL ASSESSMENT

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INTRODUCTION: Large-scale seasonal thermal energy storage (TES) substantially facilitates a full exploitation of the local renewable energy sources potential (e.g. geothermal, solar, waste heat) in renewables-based district heating systems in order to mitigate CO₂ emissions and the climate change. Large-scale seasonal TES systems store energy for long periods, thus they require large space availability: Therefore, it is essential to locate such systems properly. Accordingly, the most promising types of TES are favorably installed under the ground. It is crucial to ensure an optimal planning layout for such large-scale systems in order to avoid excessively high investment cost and performance below expectations.

To address the optimal option, it is essential to evaluate the impact of a group of key parameters on TES techno-economic performance. These parameters include hydrogeological conditions (e.g. soil type, groundwater existence and/or velocity), TES geometry (e.g. tanks, conical or pyramidal stump pits, or hybrids) and others.

MATERIALS AND METHODS: A new 3-D numerical finite-element model with multi-physics features (e.g. heat transfer, mass transfer, fluid flow) is developed in COMSOL Multiphysics to represent large-scale TES with volumes up to 2,000,000 m³ and capable to capture different geometries. By virtue of Darcy flow for porous media, the model includes the effect of groundwater temperature variations over the investigation period, ground surface temperature variations and groundwater flow with different thermo-hydraulic properties.

To obtain trust in the model, the numerical model was validated against measurements from a real-world pit TES with a volume of 60,000 m³ (Dronninglund pit, Denmark). Then, the model is cross-validated concerning the groundwater flow by means of comparing the results to FEEFLOW simulation results. Next, the work investigates the impact of groundwater velocity on TES performance. Later, the work is expanded to include the influence of groundwater longitudinal and transverse dispersion.

In this work, a Darcy flow is reduced or avoided nearby the storage structure by installing impermeable vertical physical walls forming the so-called “cut-off walls”. Cut-off walls are underground barriers at different heights to preserve the quality of groundwater and to reduce the thermal losses.

RESULTS AND CONCLUSION: Simulation results reveal a remarkable increase in the thermal losses when groundwater exists. In fact, under favorable geological conditions (i.e. no groundwater), then only conductive heat transfer from the TES to the ground occurs. Another contribution is added, which is the natural convective part, if the groundwater flow is included. Furthermore, the outcomes depict that the increase in Darcy flow velocity results into an increase in the amount of TES thermal losses and lower impact on TES temperature compared to low Darcy flow velocities. In other words, the slower the Darcy flow is, the lower the thermal losses are and the higher the groundwater temperature is.

Consequently, cut-off walls enclosing the storage are introduced to reduce the impact on and of the groundwater. The optimal distance of the cut-off wall and the required level of insulation of the TES sidewalls need to be determined by an economic optimization and depends also on the TES operation (high or low temperature district heating).

Furthermore, the influence of TES geometry is also examined under unfavorable hydrogeological conditions (i.e. Darcy flow). The corresponding results reveal that the installation of shallow pits might help in realizing lower groundwater temperature despite its low performance compared to buried tanks. Yet, it is important to highlight that the TES operation conditions might strongly influence the groundwater temperature.

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EXPERIMENTAL ANALYSIS OF A SMALL SIZE VACUUM INSULATED WATER TANK

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INTRODUCTION: The integration of thermal energy storage in solar systems is fundamental to increase the system performance and reduce the mismatch between energy supply and energy demand. Most thermal energy storage systems available for residential applications use water as a storage medium to store and supply the thermal energy required for both DHW and space heating. The reduction of heat losses helps to maintain the water in the tank at the design temperature level and enhance thermal stratification thus increasing the performance of the whole system. This paper shows the results of the experimental tests carried out on an innovative 535 litres water storage tank combined with vacuum insulation used in the EU-funded SWS-Heating project. Heat loss tests were carried out to evaluate the quality of the insulation of the tank and to calculate the heat transfer coefficient to be compared with a standard tank.

MATERIALS AND METHODS: To evaluate the heat losses of the water tank, a cool-down test was performed, preheating the tank at uniform temperature of 65 °C and recording the temperature for 48 hours. The data obtained from the heat losses test were used to calculate the U-value of the vacuum water tank to be compared with the one in the literature of a standard tank.

RESULTS: The results of the heat-loss test showed that the temperature of the middle and top layers of the tank remained almost constant during the 48-hour test. However, a large variation of temperature was observed in the bottom of the tank. Indeed, this part is only partially covered by the vacuum insulation and the connections placed in the bottom contribute to heat losses acting as a thermal bridge with the outside. The comparison with the U-value with a standard tank showed that the values calculated are significantly reduced in the top ($0.38 \text{ W}/(\text{K}\cdot\text{m}^2)$ vs. $1.05 \text{ W}/(\text{K}\cdot\text{m}^2)$) and lateral surface of the tank ($0.32 \text{ W}/\text{K}\cdot\text{m}^2$ vs. $0.66 \text{ W}/(\text{K}\cdot\text{m}^2)$). However, the bottom showed a similar value to the one of a standard water tank due the lack of vacuum insulation in the bottom.

CONCLUSIONS: The results of the heat losses test showed that the vacuum insulation allowed to maintain a high temperature in the top and the middle layers, for over 48 hours without supplying heat. This has the potential to increase the efficiency of heating systems, reducing the amount thermal energy delivered by external heat sources. However, in the design tested, the bottom is the critical part as a consequence of the lack on vacuum insulation and the thermal bridge effect of the water connection pipes.

EXPERIMENTAL EVALUATION OF A HEAT PUMP-LATENT STORAGE SYSTEM FOR INCREASING RENEWABLE SHARE OF THE RESIDENTIAL STOCK

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The primary energy consumption of the building stock in the EU is almost 40% of the overall energy consumption. Several challenges have to be tackled in order to make the energy system of the buildings of the future sustainable. Among them, increasing the self-consumption of renewables and accounting for the increasing demand in cooling are key priorities. In this context, the present paper is focused on the experimental evaluation of a reversible heat pump integrated with a latent heat storage in the evaporation circuit. The latent heat storage consists of a 3-fluids heat exchanger with passages for water (the heat transfer fluid of the air conditioning system of the building), R410 (the refrigerant of the heat pump) and a commercial paraffin with nominal melting temperature of 4 °C, which is the storage medium.

Aim of the experimental campaign was the evaluation of achievable performance of the heat pump under variable temperature levels, corresponding to operating conditions in different places of installation and boundaries. The charge and discharge processes of the storage were characterized to identify the energy capacity, achievable power and time to complete the process. Different operating modes for the system coupling heat pump and latent storage were tested, namely operation of the heat pump only, charge of latent storage, discharge of latent storage and parallel charging/discharging of the storage. Moreover, the heat pump was modified in order to drive the compressor with DC current and different speeds of the compressor of the heat pump were tested, to identify the effect on the EER (Energy Efficiency Ratio= cooling output/electricity input) and on the charge of the storage.

The results indicated that the heat pump works with EER from 3 to 7 for ambient temperatures of 40°C to 20°C and the EER increases for part load operation for the lower ambient temperatures. Regarding the operation of the latent storage, the effect of heat transfer fluid flow rate proved to be central in the time needed to charge the storage (the higher the flow rate the lower the time needed to charge the storage) and for the amount of energy recovered, that has an optimum at 0.15 kg/s.

Finally, the results of the tests were used to derive simplified correlations able to describe the operation of the storage, for implementation in artificial intelligence-based algorithms.

REVIEW OF THERMAL ENERGY STORAGE IN HEAT PUMP SYSTEMS FOR HEATING AND COOLING

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The popularity of heat pumps stems from their ease of use and the possibility of bringing low-temperature heat sources to a higher temperature. This means they can use low-grade renewable energy sources (such as air, water, ground, solar) as well as waste heat sources to reduce the demand for fossil fuels and thus reduce greenhouse gas emissions. Their big advantage is that they can be used for heating and cooling, even simultaneously. This means that virtually no heat is dissipated, making such systems truly efficient. However, it is necessary to install thermal energy storage (TES) units so that their operation is more continuous and economical. In this article are therefore presented different kinds of heat pump systems for heating and cooling (focus on air and ground) of buildings that have integrated thermal energy storage (TES) either in the form of water (ice), ground and phase change material (PCM). Focus is on the impact of TES implementation on the system operation, energy efficiency and cost-effectiveness. Results from different studies are compared in terms of COPs, TES sizes, storage media, performance indicators.

MODELLING VERY LARGE THERMAL ENERGY STORES - COMPREHENSIVE COMPARISON OF DIFFERENT MODELS

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INTRODUCTION: Large-scale thermal energy storages (TES) are advantageous to bridge the seasonal gap between the heat demand and availability of renewables, thus eliminating any mismatch. However, the high investment costs associated with large-scale TES is still seen as a major obstacle. Major challenges in large-scale TES realization are space availability and the presence of groundwater tables. Thus, simulation-based analyses found their place in the planning phase of such large-scale systems due to the complexity of the process (Ochs 2018, Ochs et al. 2019, Ochs et al. 2020).

METHODS: A pre-design tool can be useful in the early TES planning phase to examine the potential. Details have to be systematically included in the TES model for a detailed TES design. In order to examine the integration of TES into a specific (renewable) district heating system, energy system tools are required. As a result, the technology is thoroughly evaluated and the outputs (energies and temperatures) are post-processed in the evaluation level. If the planners are not yet satisfied with the results, then TES planning reaches to the optimization level whereby different parameters (e.g. volume, construction type, insulation thickness, etc.) are examined.

For very large-scale TES intended for application in district heating systems, different TES types and geometries can be considered. Within this work volumes ranging from 100 000 m³ up to 2 000 000 m³ are investigated. The TES types and geometries include buried tanks, pits and hybrids: Tank (Cylinder, Cuboid), pit (truncated cone, pyramid stump), Hybrid (cylinder with cone stump, cuboid with pyramid stump). TES can be built completely buried (underground) or partially buried building a dam with (part of) the excavated soil. Depending on the ground properties and presence of ground water and operation conditions (i.e. high temperature or low temperature) different levels of insulation will be necessary and/or favourable.

For the TES optimisation, flexible and detailed TES models are required that allow for different geometries, insulation levels and boundary conditions (e.g. presence of ground water) to be investigated. Contrariwise, for system simulations, fast and easy to use models are required. Within this work, different TES models are compared. The tools included in this comparison are COMSOL Multiphysics (Dahash et al. 2020), TRNSYS (Types 1300/1301, 1322 and 342, Klein et al. (2006)), Modelica/Dymola and Matlab/Simulink (Ochs, 2014).

The detailed 3D FE model developed in COMSOL Multiphysics was validated against measured data from a pit TES in Denmark and is used as a reference (Dahash et al. 2020). Some of the models make use of symmetry and cylindrical coordinates in order to reduce the model to 2D (cylinder, cone). In case of a cuboid or pyramid stump, a 3D model can be reduced to a quarter using symmetry again. In both cases, the influence of ground water cannot be considered.

RESULTS: The features of the different TES models are summarized and the different concepts to reduce the model complexity are shown. The results with respect to thermal losses, temperature stratification and computational performance are compared. A variety of TES tools is available. The comparison of the results showed initially significant deviations, which can be explained by both user influence and also model inefficiencies. Models could be improved and user influence excluded. All tools can predict the performance

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with sufficient accuracy, while the modelling effort, the flexibility of use and the computational effort is significantly deviating.

CONCLUSIONS: The comparison focuses on the TES as a stand-alone component using different charging and discharging profiles. In a second stage the comparison will be extended to system level and include control. The comparison will be further extended in the framework of the collaboration within IEA ECES Annex 39.

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RADIAL DIFFUSERS WITH TWIST GENERATION FOR ARROW STORAGE TANKS – FIRST EXPERIMENTAL STUDIES

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The loading of narrow thermal energy stores with radial diffusers is associated with fluid mechanical effects that make it difficult to create thermal stratification. This paper presents the use of guiding elements in the diffuser, which should generate a twisted charging stream. The aim is to influence the stream in such a way that the thermal stratification is improved. Preliminary investigations with the help of CFD simulations show that a reduction of maximum velocities by means of jet deflection is particularly beneficial. Based on this, first experimental investigations with different charging device geometries and volume flows as well as wall distances were carried out. The direct comparison between variants with and without twist generation was in particular focus. The results show only partial advantages of the charging devices with twist generation and do not fully confirm the results of the simulation. There are various reasons for this.

In the experimental investigations, scaling effects occur. Due to these effects, the results and findings for the different charging devices and storage sizes are not fully transferable. In order to reduce these effects, the model store should be increased. The decreasing values for $h\dot{U}S$ with increasing volume flows also indicate a significant influence of the heat losses through the thin, uninsulated store wall of the test rig. The influence is particularly significant at low volume flows. The installation of thermal insulation would be advantageous here. The difference between the variants with and without twist generation at higher volume flows is possibly greater. An investigation with $V > 3,0 \text{ m}^3/\text{h}$ is still pending. Furthermore, no variation of the angle of twist generation ($\beta = 50^\circ$) has been carried out so far. Optimizations are also possible here. A key role is played by a better understanding of the processes in the diffuser and near the outlet.

Based on these and further investigations, promising variants are to be selected, examined in detail and transferred into practical application in the future. For this purpose, additional economic and constructive analyses are necessary.

ECONOMIC OPTIMIZATION OF SEASONAL THERMAL ENERGY STORAGE SYSTEMS

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INTRODUCTION: Space and water heating are responsible for a large portion of the energy needs of buildings: about 80% in Europe and 62% in United States. In combination with seasonal thermal energy storage (STES), renewable energy technologies offer a vast potential for the supply of hot water and space heating. Today, increasing market diffusion of STES requires reducing the investment costs, especially when it comes to small-scale storages integrated inside buildings. In this work, we perform an economic optimization of a STES system comprised of a stratified hot-water storage combined with a solar thermal installation. Two scenarios are considered: (1) a storage integrated inside a residential building, and (2) a storage buried underground in direct vicinity of the building. Boundary conditions for the storage are volumes in the range of 100 – 250 m³ and temperatures up to 90 °C.

MATERIALS AND METHODS: A system optimization is performed using an in-house transient numerical model that describes the stratified hot-water storage, the solar thermal collector installation and a multifamily low-energy building. The system is designed such that the total heating demand is exclusively covered with solar heat. A parametric optimization is carried out to minimize the Levelized Cost of Energy Storage with 100% autarky (LCOES100) by varying the thermal insulation material and its thickness, the storage diameter and the solar collector area.

RESULTS: By integrating a hot-water storage as part of a retrofitting inside an existing residential building – where costs are primarily driven by loss of living space –, maximizing the solar collector area is the best strategy to minimize LCOES100. In the retrofitting scenario, vacuum-insulation panels (VIP) – as an alternative to conventional glass wool – can lead to 20% savings in living space and a cost advantage of about 5%. At an LCOES100 of about 1.0 EUR/kWh, the integration of the storage inside an existing building is the most expensive option due to high costs associated with the internal modification of the building and loss of living space. The LCOES100 can be reduced by 50% if the storage is integrated inside a new building – mainly because of the high building reconstruction costs that are avoided. In spite of the high excavation costs and increased heat losses, the concept of burying the STES underground represents a promising option (LCOES100 ~0.5 EUR/kWh) to allow integration of seasonal storage systems in both new and existing residential buildings.

CONCLUSION: We showed that a retrofit with a thermal storage is economically unfavorable and that burying the storage is preferable despite the high excavation costs. Thus, commercially available vacuum-insulated storages seem to be a promising solution for retrofit applications, as they offer the possibility of avoiding the high penalty costs associated to loss of living space and internal reconstruction of the building that is required when placing a large-volume tank inside an existing building. Moreover, a storage buried underground avoids additional heating of the building during the summer season that results from the unavoidable heat losses from the storage to its surroundings.

BUILDING A PREDICTIVE MODEL FOR A HEAT SOURCE SYSTEM WITH THERMAL ENERGY STORAGE USING MACHINE LEARNING

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INTRODUCTION: Recently, the optimal operation of heat source systems has invoked model predictive control (MPC) to reduce energy consumption and costs. MPC consists of two parts; an optimizer and a predictive system. The efficiency of MPC is influenced by the accuracy of the predictive system. Modeling methods are roughly classified into white-box and black-box models. A white-box model is based on physical laws, whereas a black-box model relies on statistical methods. In general, a black-box model is faster at calculating heat source system behavior because it does not require iterative calculations. Thus, it is expected that a black-box model will be widely used for real time control. However, it is required that its' prediction accuracy should be confirmed. Machine learning is one of representative methods that make a black-box model. In this paper, machine learning hyper-parameters are compared for a high-accuracy model predicting the behavior of a heat source system with thermal energy storage (TES).

MATERIALS AND METHODS: The modeling target is a system containing an air-source heat pump chiller, TES, pumps, a heat exchanger that mimics a fan coil unit and a water tank that replaces actual air conditioning space. Cooling load is obtained by an electrical heater which is installed in a water tank. This system has several control strategies. One is to operate storage and chilling equipment through 4 modes; charging mode, discharging only mode, discharging and chiller mode and chiller only mode. Charging mode is invoked for fixed periods via schedule control. In addition, an inverter is installed in each pump to control water flow rate at a water temperature setpoint. Measurement data is logged through an accelerated experiment that shortens a day from 24 hours to 4 hours; in other words, 10 min of actual time corresponds to 1 hour (60 min) of virtual time. Measurement and model predictive periods are set for 1 min of virtual time. Predictive models of the heat source system were built using a feed-forward neural network with more than three layers including input and output. The input information consisted of 32 points including 12 water temperature, 6 water flow rate, outside air temperature and humidity, laboratory room air temperature, power consumption of chiller, 5 pumps and electrical heater, and 4 operating modes that were ON or OFF. Output information from the predictive models were forecasted values after 1 step, consisting of 18 points including water temperatures and power consumption of the chiller and pumps. A back-propagation method was used to train models and the Adam algorithm was applied. An RMSE (Root Mean Square Error) loss function was also used to train models. To compare model performance, MAE (Mean Absolute Error) produced from 1440 recursive steps of the model simulating behavior of a heat source system based on test data was applied to an evaluation index. The machine learning data was equivalent to 25 days, 90% of which was used as training data with the remaining 10% for validation data. In addition, test data equivalent to one day was available. All machine learning and test data was preprocessed for each item using min-max normalization to avoid influence from different characteristics between temperature and power consumption. Case studies on hyper-parameter hidden layers, number of hidden nodes and input information were conducted. Specifically, the hidden layers contained 1 to 5 layers, with the number of each hidden layer nodes being 50, 100, 500 and 1000, and the sequences, which corresponded to the amount of historical data input into the models, consisted of 1, 15, 30 and 60 steps. Therefore, 80 conditions were compared to evaluate the predictive accuracy of models.

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RESULTS: The relationship between each hyper-parameter and the predictive accuracy of models in the simulator was evaluated, with the results shown below. Predictive accuracy improved as the number of hidden layers and number of sequences increased, and better predictive accuracy was obtained for 4 layers and 60 steps compared to other conditions. While predictive accuracy was slightly influenced by the number of hidden layer nodes, an equable trend was not confirmed. In the results, the hyper-parameters obtaining the highest predictive accuracy of the model were 4 layers, 50 nodes and 60 steps, with an MAE of 0.0452 calculated using min-max normalization. The calculation time for the model to simulate the heat source system behavior up to 1440 steps was 15.4 sec using an off the shelf computer (CPU: 3.60 GHz (4 cores), RAM: 32 GB). The calculation time to train the model was 876 sec. Thus, it was shown that the feed-forward neural network set with appropriate hyper-parameters could be used as a simulator with high predictive accuracy.

CONCLUSION: In this paper, a model was built using feed-forward neural networks based on actual data to predict the behavior of a heat source system, and its predictive accuracy was evaluated. In the results, the model showed high predictive accuracy as a simulator when hyper-parameters were set to appropriate values. Therefore, it is expected that a model built using this method can be applied to MPC to realize real-time optimal control and reduction of energy consumption and operation costs.

TEMPERATURE DISTRIBUTION ON DIRECTLY IRRADIATED SPOUTED BEDS

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Fluidized beds have a huge potential in CSP applications. Their high mixing rates and heat and mass transfer coefficients make them the most suitable fluid-particle technology for distributing a high flux of concentrated solar energy throughout a whole group of particles. One key aspect to properly study in a beam down reflector using a fluidized bed as receptor and storage system is the maximum temperature reached by the solid particles on the top of the bed, which are directly exposed to the concentrated radiation, especially at the center of the bed. Very high temperatures that could cause severe sintering and attrition problems.

In a recent work (Díaz-Heras et al. (2020). Experimental observations on directly irradiated fluidized beds: even and uneven fluidization. *Experimental Thermal and Fluid Science*, 110242.) the authors have presented experimental measurements in a bubbling fluidized bed. A thermographic camera was used to measure the particle temperature distribution on the top surface of a fluidized bed varying the height of the bed and the airflow rate. In addition, two different flow distributions were analysed: 1) a uniform flow distribution through the whole cross-section of the bed (even fluidization), and 2) a non-uniform flow distribution, with a higher flow rate at the central region of the bed (uneven fluidization). The second case presented similar or even lower temperatures in the bed than those given with a lower airflow rate, requiring lower pumping costs.

Following this research line, this paper presents similar experimental data obtained in a conical spouted bed with SiC particles. In this type of bed, the main flow is introduced through an orifice or a spout at the bottom of the bed. The particles are transported to the top forming a fountain when they reach the surface, being subsequently recirculated into the annular region. Spouted beds permit to “fluidize” large particles belonging to Geldart D group (particles with a diameter up to a few millimetres) with a reasonable airflow rate. The study covers variations in the airflow configuration: introducing the air stream only through the spout of the bed, and also introducing air through the annular region of the bed. The main objective of this study is to find the optimum airflow distribution which minimizes the peak temperatures observed in the particles directly radiated to avoid attrition and sintering problems. The results will be also compared with the results obtained in our previous work with even and uneven fluidization.

BUSINESS CASE IMPROVEMENT OF A MULTI-ENERGY PLANT CONTAINING A WOOD BOILER, AN ORGANIC RANKINE CYCLE AND TWO THERMAL ENERGY STORAGE VESSELS

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INTRODUCTION: A wood joinery in Belgium has decided to use a combination of a waste wood boiler, an ORC (Organic Ranking Cycle, CHP unit) and two storage vessels to maximize the self-sufficiency in heat and electrical energy using the locally available waste wood. The integration of thermal energy storage is important for unlocking the flexibility of the system and allowing for smart control: in this case the consumption of locally produced electricity can be increased during periods when electricity prices are high to gain an economic benefit.

MATERIALS AND METHODS: The installation has been monitored from September 2016 till March 2020. The monitoring focused on the thermal energy flows in different locations of the installation as well as the electrical energy flows. Results show that the estimated heat demand during the design phase was considerably higher than the one measured during the monitoring period, meaning that the installation was oversized. Consequently, the potential of the thermal storage was not fully exploited. As the wood joinery is located in an industrial area, the potential of using the heat production installation to provide heat to nearby companies via a district heating network was investigated to improve the business case of the installation. For this reason, a detailed mathematical model of the multi-energy plant has been developed. The measured site plant heat and electric demands of 1 year was used along with multiple theoretical demand profiles to emulate potential heat demand scenarios from nearby companies. Particularly, the measured heat demand was scaled up to represent different external heating demand profiles leading to an increase in the usability of the thermal storage. The goal of each simulation was to evaluate the economic benefit of each scenario, assuming the plant is running under the optimal control conditions (i.e. the ones which minimize the running cost while maximizing the revenues). In order to find the optimal control sequence for each scenario, a detailed linear mathematical formulation of the site plant was developed, which allows the application of a constrained linear programming optimization. In particular, the controlled variables were: (i) the boiler generation power, (ii) the energy stored/released by the two thermal storage vessels and (iii) the electrical power generation of the ORC. The cost has been computed as the total electricity bought from/sold to the grid while satisfying the entire heat demand (i.e. both internal and external) through the full simulation period of 1 year. In order to evaluate realistic scenario costs, the energy tariffs have been extrapolated using the plant site bills, including peak and off-peak periods. For the district heating network, realistic heating tariffs have been considered as well as realistic maintenance and investment costs in order to compute the heating revenues. This mathematical model has been developed in Python language, using Gurobi optimizer as an optimization solver.

RESULTS: The heat demand upscaling demonstrated that, with the current installation, an extra thermal consumption up to three times the current consumption (with a similar profile) can be added without the need to upgrade the installation. For an upscale of the heat demand with a factor of 3.6, the simulation showed that with the current storage tanks in the system and using the control strategy aiming to maximize the electricity production, the owner saves 9% on the electricity bill compared to the base case, without thermal energy storage. Moreover, the economic feasibility of connecting the nearby companies to the

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wood joinery via a district heating network was investigated. Results showed that for a heat price in the range of 17.5 and 70 Eur/MWh and a district heating installation cost in the range of 195 and 780 Eur/m, the payback period ranges between 10.4 and 0.6 years in the worst- and the best-case scenarios respectively.

CONCLUSION: This study demonstrated the importance of evaluating a system after installation through continuous detailed monitoring. As in this case, the monitoring showed that the installation is oversized as the heat demand is lower than estimated initially. Consequently, the simulations concluded that with the use of thermal storage, the business case of the installation can be considerably improved if heat can be sold via a district heating network connecting nearby companies.

A STUDY OF SPACING EFFECT ON POOL BOILING PERFORMANCE OF THREE TRIANGULAR PITCHED AND VERTICALLY ORIENTED TUBES

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INTRODUCTION: Mobile thermal energy storage (M-TES) systems have been proposed in order to connect a waste heat supplier with a consumer when pipe-line connection is economically not feasible. Such systems can be more efficient and feasible by means of phase change materials (PCMs) to store thermal energy [1] even when utilizing low or medium potential waste heat. Deckert et al. [2] have been shown that not only the storage capacity, but also charging and discharging rates play an important role in the economical efficiency of such systems. Thus, more efficient methods to charge and discharge M-TES system that may significantly increase the number of operating cycles per year have to be explored.

Pool boiling provides much higher heat transfer coefficients (HTC) compared to convective and heat transfer under evaporation. A discharge of M-TES systems can be realised by means of pool boiling similarly to flooded shell and tube heat exchangers i.e., the encapsulated and submerged in working fluid PCM capsules, will serve as a heat source. However, optimisation of M-TES systems energy density and discharge rate require experimental data on pool boiling heat transfer at target conditions. In spite of a significant number of studies focused on the boiling on tubes bundles, this process is not fully explored. Most of the published papers are dealing with horizontal tubes bundles [3], rather than with vertically oriented. Nonetheless, vertically aligned tubes may have higher HTC compared to horizontal arrangement under similar conditions.

Thus, the aim of this study is to get a set of experimental data regarding the effect of spacing on pool boiling of vertically oriented tube bundle. Subsequently, those data will be used to verify CFD modeling of boiling heat transfer in a similar tube bundle configuration that finally will be used to optimise heat storage capacity and discharge rate of M-TES systems.

MATERIALS AND METHODS: A custom made experimental setup was created to perform the study. It provides visual access to the geometries with up to $L=150 \times H=150 \times W=50$ mm in size. The test section was made out of three capillaries (AISI 321), having 2 mm in outer diameter, 0.1 mm in wall thickness, 130 mm in length and L/D ratio of 150. Four thermocouples were installed in each capillary in order to measure the local temperature distribution and HTC along their height. Four spacing of 10.75, 6.25, 1.75 and 0.25 mm were tested with ethanol as working fluid at 78 °C in the range of heat flux density from 3 to 70 kW/m². A high speed camera i-SPEED 210 from IX-cameras was used to capture the boiling process at 800 fps.

RESULTS: The long spacings of 10.75 and 6.25 mm show identical results in a sense of HTC and bubble dynamics revealing that there is no significant interaction between the capillaries and bubbles. Such bundles behave similarly to the single tubes. Further reduction of spacing to 1.75 mm has caused slug flow on the bubbles nucleated in the gap created by three capillaries at low heat flux density. This effect may enhance HTC up to two times at fixed wall superheat and up to 20% at fixed heat flux density. In the mean range of heat flux 20-45 kW/m² the HTC at this spacing perform similarly to that of 10.75 and 6.25 mm, revealing that the process of bubble nucleation is dominant among others. However, at heat flux density higher than 45 kW/m² the bubbles tend to coalesce that reduce the vapor removing rate and consequently reduce the HTC. At the shortest spacing of 0.25 mm the bubbles are significantly larger due to coalescence and higher energy density in the gap between the tubes that increase the vapor generation rate. The HTC is always higher at this configuration at the bottom part of the bundle (up to 55 mm of height)

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Short oral lectures/posters

due to stronger turbulence produced by larger bubbled. However, above 55 mm of height large bubbles create vapor blankets that deteriorated HTC.

Besides that, the other effect was captured. The bubbles are creating a "flambeau"-like or "cone"-like shape along the tubes height that is turned by its apex to the base of the tubes bundle. This effect caused by the interaction between floating up bubbles and the bubbles on the stage of nucleation and departure. During the nucleation and departure from the vertical surface bubbles have an impulse in a horizontal plane that is consequently can be transmitted to the nearest bubbles. Hence, the observed "flambeau" effect is stronger at higher heat fluxes and shorter spacings, when the number of active nucleation sites is high and they are close to each other. Nevertheless, the "flambeau" effect tends to reduce the interaction between the vertical surface and bubbles and its impact on heat transfer is insignificant.

CONCLUSION: Boiling process on a simplified tube bundle consisting only of three tubes has been studied. Long spacings of tubes are not influencing the boiling process. However, short spacings may enhance or deteriorate the HTC depending on the parameters. The spacing that promote slug flow is very beneficial for the heat exchangers working at low heat fluxes. The spacings that are much shorter than the bubble departure diameter are potentially very beneficial for the tube bundles with low L/D ratio. It is clear, that the heat exchangers with a constant spacing of tubes may be optimal only in the narrow range of parameters. The increase of the efficiency of the heat exchangers working in the wide range of parameters requires more sophisticated design like bundles with variable tubes spacing and/or tubes diameter.

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VALIDATION OF NUMERICAL MODEL FOR LATENT THERMAL STORAGE OPERATION AND ANALYSIS OF HEAT CHARGE AND DISCHARGE IN TRNSYS

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A convenient solution to increase energy density of conventional water thermal storage is with the use of encapsulated phase change materials that can be installed in the existing water tank through a flange. That kind of solution brings quick and pragmatic solution of energy density improvement but it leads to more complicated operation of thermal storage from state-of-charge point of view. The simulations can help in better understanding of thermal storage operating conditions. That is why the focus of present research is on simulations under different initial conditions with numerical model that was validated with measurement results. The investigation took place on water thermal storage tank with encapsulated phase change materials (PCM) that represented 30% of the thermal storage volume. The measurements of a 100 l water tank with 190 spherical capsules filled with PCM (hydrate salt mixture) were performed. The numerical model for latent thermal storages was used in TRNSYS environment and was adjusted according to the boundary and initial conditions of the experimental system and measurement conditions. The results of simulations were compared with the measurements in order to perform the validation of the numerical model. After successful validation, the simulations of different initial water temperatures to the thermal storage system were made in order to analyse its heat charge and discharge process.

DEVELOPMENT AND ANALYSIS OF A CFD RESULTS BASED SYSTEM SIMULATION MODEL FOR A LATENT HEAT THERMAL ENERGY STORAGE UNIT WITH MACRO-CAPSULES

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INTRODUCTION: Macro-encapsulation of phase change materials (PCM) is a successful approach to improve the performance of latent heat thermal energy storage systems (LHTESS). The design process of LHTESS is complex and is therefore increasingly supported by numerical simulations. The numerical models applied can be divided into system simulation models and Computational Fluid Dynamics (CFD) models. CFD models enable to describe the solidification and melting processes in macro-capsules in detail. A major drawback is that it takes several hours or even days to compute the phase change of the PCM in a single capsule. For this reason, models for system simulations rely on highly simplified approaches, the most common one being based on strong simplifications of the physical processes. For example, natural convection and the sinking of the solid PCM are neglected. Since this approach is highly imprecise, we present an approach that uses data from CFD simulations to create a simplified model suitable for system simulations. The approach is presented and analyzed for the charging i.e. melting of the PCM in a LHTESS with horizontal cylinders.

MATERIALS AND METHODS: The idea of the approach is to perform a series of CFD simulations with different temperatures of the capsule inner wall. From these simulations a two-dimensional look-up table is generated which lists the currently transferred heat as a function of the internal wall temperature and the stored thermal energy. The CFD simulations are performed in OpenFOAM with a previously developed and validated solver. The system simulation model was created in MATLAB Simulink and uses a one-dimensional discretization for the heat transfer fluid (HTF). It accounts for the capsule wall and accesses the created look-up table to describe the heat transfer inside the macro-capsules. The heat transfer from the HTF to the capsule wall is considered by correlations. This modeling approach relies on several assumptions/simplifications. The main ones are:

- The heat transfer in the PCM is only a function of the stored thermal energy and the inner wall temperature.
- The capsule wall is isothermal.
- The flow and the heat transfer in the HTF can be described with a simple one-dimensional approach.

RESULTS AND CONCLUSION: Whether the first assumption is appropriate is checked in detail in this work. For this purpose, results of the system simulation model are compared with CFD simulations in which the inner wall temperature is varied over time. The temperature jumps occur in positive and negative direction to a then again constant temperature and are varied in height, time and gradient. Although, especially for large negative jumps with a high gradient, quite large deviations in the transmitted power can occur for a short period of time, for jumps of 20 K the average deviations are always below 5 %. Interestingly, the slope of the jump has a large influence on the maximum deviations but almost non on the mean deviations. A future research project at the University of the Basque Country aims to pursue this model approach and to develop new approaches based on projection methods.

EXPERIMENTAL STUDY OF A NOVEL THREE-FLUIDS HEAT EXCHANGER EMBEDDED WITH PHASE CHANGE MATERIALS FOR COOLING APPLICATIONS

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INTRODUCTION: According to the international energy agency (IEA), the buildings sector needs to reduce its energy consumption and CO₂ emissions by over 70% in comparison to 2010 levels in order to limit the increase of global temperature. Strategies to use renewable energy sources are suggested, but due to the mismatch between energy production and consumption, the use of energy storage systems is one promising way to address this issue. However, implementing energy storage into systems means additional components, costs and complexity of the systems. To respond to these challenges, a novel 3-fluids refrigerant-phase change material (PCM)-water heat exchanger (RPW-HEX) designed by AKG (Germany) was designed and experimentally investigated in a vapour compression system replacing the conventional evaporator within the EU-funded HYBUILD project.

MATERIALS AND METHODS: The novel heat exchanger was designed to incorporate refrigerant, PCM, and heat transfer fluid (HTF) in adjacent channels, allowing heat transfer amongst each other as well as cold storage in a single compact device, thereby eliminating the need of additional components. An amount of 3.15 kg of commercial RT4 was used as PCM, and a mixture of 30% glycol by 70% water was used as HTF. Several experiments were performed to study the performance of the RPW-HEX in three operating modes: charging, discharging of the RPW-HEX, and direct heat exchange between the refrigerant loop and the HTF loop. A parametric study was performed to assess the influence on different parameters on the latent energy storage and heat transfer rate.

RESULTS: In charging mode, the RPW-HEX could only be charged partially due to the non-uniform temperature distribution. Increasing the cooling power led to an even less uniform charging though it reduced the charging duration. A maximum amount of 964 kJ was charged in the RPW-HEX, which accounts for only 89% of its maximum theoretical storage capacity at set-point condition. The discharging process duration was reduced by increasing the HTF flowrate or by increasing the HTF inlet temperature. It took 25 minutes to completely discharge the RPW-HEX with HTF flow rate at 50 L·h⁻¹ while taking only 9 minutes with HTF flow rate at 150 L·h⁻¹. For the direct heat transfer between the refrigerant loop and the HTF loop through the RPW-HEX, the energy stored is dependent on both cooling power and the HTF flow rate, and it is higher when using higher cooling power and/or lower HTF flow rate.

CONCLUSIONS: In this study, an experimental testing of a novel 3-fluids heat exchanger directly integrated into a simple refrigeration system was performed. A parametric study was performed to assess the influence of the main parameters in three modes, i.e. charging, discharging, and direct heat transfer between two loops through the RPW-HEX. The study concludes that the novel 3-fluids heat exchanger is a feasible solution to implement thermal energy storage into refrigeration/air-conditioning systems resulting in a compact and less complex system.

LONG TERM PERFORMANCE EVALUATION OF LARGE SCALE ATES FOR COMMERCIAL BUILDINGS: CASE STUDY IN STOCKHOLM

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ATES systems have proven to be one of the most effective methods for sensible thermal energy storage and been increasingly used for seasonal and short-term storage. The majority of ATES systems studied are conducted in ATES systems located in large sand aquifers. The aim of the current study is to evaluate an ATES system located in an esker geological formation which is more challenging from a geometrical complexity point of view. The thermal and hydraulic performances are evaluated for the first three years of operation of an Aquifer Thermal Energy Storage (ATES) in an esker located in Stockholm, Sweden. The ATES is of a doublet well type that consists of two groups of wells, warm and cold. The ATES is used for both heating, as a source for two ground source heat pumps, and free cooling with average yearly energy exchange of 160 MWh and 250 MWh for heating and cooling respectively. The licensed total amount of water extraction and injection is 50 liters per second. The undisturbed aquifer temperature is 9.5°C and has been measured during the summer of 2016 before the start of the first ATES operation cycle using distributed temperature sensing (DTS) equipment. The average injection and extraction temperatures for the warm side are 15°C and 13.5°C, and for the cold side 7.5°C and 12°C. The average temperature differences across the main heat exchanger are 4.5K during winter and 5K during summer. When analyzing the monitoring data, the average thermal energy ratio for the warm and cold storage sides are 0.52 and 1.66. The thermal recovery efficiency, defined as the amount of recovered energy from the net energy previously injected to warm up or cool down the ATES, was ranging between 38%-11% for the warm storage. This was mainly due to the lower heating demand and lack of heat extraction from the warm storage side during the last two operation cycles. The ATES system showed an unbalanced operation during the first three years, using increasingly more energy as well as water volume for cooling than for heating. Furthermore, temperature differences during heating and cooling operation has been 2-6 degrees lower than the optimal values which lead to occasional injection temperature lower than the ambient groundwater temperature in the warm side and higher in the cold storage side. The lowest extraction temperature from the warm storage was around 12°C due to the lowered heating demand. The extraction temperatures from the cold storage side during cooling operation has increase from 6°C in the first cooling cycle up to 13°C near the end the last cooling cycle. This indicated a suboptimal interaction between the two wells' groups and thermal breakthrough that led to an overall increase of the ATES temperature compared to the undisturbed groundwater temperature. The relatively suboptimal utilization of the ATES is attributed to the decreased heating demand due to warm winters in the later years as well as inefficient operation control, which leads to using more heat from district heating instead of the ATES coupled heat pumps in addition to suboptimal operational temperature differences. Further operation optimization for the ATES taking into account both the building HVAC and ATES KPIs is needed in order to ensure more sustainable operation of the system in the future.

CHEMICAL IMPACTS OF SHALLOW AQUIFER THERMAL ENERGY STORAGE: STATISTICAL ANALYSIS FOR FIRST YEAR OF OPERATION OF STUDY CASE IN SWEDEN

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Underground Thermal Energy Storage (UTES) systems, such as Aquifer thermal energy storage (ATES) are used in several countries. The regulation and research on the potential impacts of ATES on groundwater resources and the subsurface environment often lag behind the technological development of an ever-growing demand for this renewable energy source. The lack of a clear and scientifically supported risk management strategy implies that potentially unwanted risks might be taken at vulnerable locations such as near well fields used for drinking water production. At other sites, on the other side, the application of ATES systems is avoided without proper reasons. This results in limiting the utilization of the ATES technology in many occasions, affecting its market share. Therefore, further studies to identify environmental impacts is needed to understand the advantages and limitations of ATES systems from this perspective.

This paper presents the impact on groundwater chemistry from a Low Temperature ATES (LT-ATES) system that has been operational since 2016. The system is located in the northern part of Stockholm, on a glaciofluvial deposit called the Stockholm esker.

Analysis of groundwater sampling included a period of 9 months prior to ATES operation as well as the first full season of heating and cooling operation. The sampling was conducted in a group of wells in the vicinity of the installation and within the system as ATES operation began. Means of evaluation constituted a statistical approach that included Kruskal-Wallis test by ranks, to compare the wells before and after the ATES was used. Then principal component analysis (PCA) and clustering analysis were used to study the ground water conditions change before and after the ATES. Aquifer Variation Ratio (AVR) was suggested as mean to evaluate the overall conditions of the aquifer pre- and post- ATES.

The analysis was based on foremost the cycle of cold energy storage. The results showed some variations in redox potential, particularly at the cold wells which likely was due to the mixing of groundwater considering the different depths of groundwater being abstracted/injected from different redox zones. Arsenic, which has shown to be sensitive to high temperatures in other research showed a decrease in concentration. There were found to be a lower specific conductivity and total hardness at the ATES well compared to their vicinity. That indicates that they are less subject to salinization and that no accumulation has occurred to date. It is evident that the environmental impact from ATES is governed by the pre-conditions in soil- and groundwater. The PCA and clustering analysis showed very little change in the overall conditions in the aquifer when comparing the ATES before and after operation. Temperature change showed negligible impact. This can be mainly attributed to the relatively small temperature change (6 degrees) from the undisturbed Aquifer temperature which is 9.5°C. It is likely that the temperature difference will increase with time and therefore a follow up study for the following two heating and cooling seasons is planned.

FORMATION MECHANISM OF Al@Al₂O₃ CORE-SHELL TYPE MICROENCAPSULATED PHASE CHANGE MATERIAL

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INTRODUCTION: A latent heat storage system using phase change materials (PCMs) is a promising technology to apply in grid-scale high-temperature thermal energy storage (HTTES), which is essential to extend renewable energy utilization. Recently, Al@Al₂O₃ core-shell type microencapsulated PCM (MEPCM) is developed for HTTES [1]. Since MEPCM has high heat storage capacity and thermal conductivity, HTTES using MEPCM is expected to have higher performance than conventional HTTES using sensible heat storage material. Al@Al₂O₃ MEPCM was synthesized in simple and easy two steps: (1) boehmite formation on the particle surface by boiling and (2) heat-oxidation treatment. This method can be applied to alloys with various melting points, including Al as a component [1, 2]. However, the detailed oxidation mechanism of forming the Al₂O₃ shell is unclear. Elucidation of the formation mechanism of Al₂O₃ shell is essential to produce the high-performance MEPCM more efficiently. Therefore, the purpose of this study is to clarify the oxidation mechanism during MEPCM synthesis. This study can control the structure of the Al₂O₃-shell and optimize the thermal properties, strength, and synthesizing process of MEPCM.

MATERIALS AND METHODS: Micro-spherical particles of Al prepared by disk atomization method (purity:99.7% Hikari Material Industry Co. Ltd.) were used as a raw material. Al has a melting point of 660 °C. First, the raw material was boiled in distilled water for 1 hour. The water temperature was then cooled to 75 °C and kept for 16 hours to form boehmite (AlOOH) on Al particles. Then the sample was filtrated and dried at 110 °C overnight. Finally, the boehmite-treated samples were subjected to heat-oxidation treatments under O₂ or Ar flow of 200 ml min⁻¹ with a thermogravimetry analyzer (TGA, Mettler Toledo TGA-DSC-3). The sample was heated from room temperature to 1100 °C at a rate of 10 K min⁻¹. Thus, the boehmite film transformed to Al₂O₃. The sample's phase compositions for each treatment were characterized by powder X-ray diffraction (XRD, Rigaku Miniflex, Cu Ka), whereas its morphology for each treatment was observed by scanning electron microscopy (SEM, JEOL, JSM-7001FA).

RESULTS: In XRD patterns of the samples after boehmite treatment, Al, AlOOH, and Bayerite (Al(OH)₃) were detected. SEM images of the samples after boehmite treatment that AlOOH and Al(OH)₃ were obtained.

In XRD patterns of MEPCMs after heat-oxidation under O₂ atmosphere, Al and Al₂O₃ were detected. SEM results show that Al₂O₃ with boehmite-derived flower-like nanostructure was obtained on the surface of the sample. Furthermore, a band-like structure of Al₂O₃ was observed on the surface. The weight change during heat-oxidation under O₂ atmosphere measured by TGA is divided into 4 phases: (1) weight decrease from starting weight to 89.60% just before melting point, (2) rapid weight increase to 89.95% just after melting point, (3) rapid weight increase to 93.64% between 850 °C and 1000 °C, and (4) gradual weight increase to 93.88% between 1000 °C and 1100 °C. These phenomena are (1) dehydration of AlOOH, and Al(OH)₃, (2) rapid oxidation of Al exposed from cracks generating by volume expansion of solid-liquid transformation of core-Al, (3) rapid oxidation of Al in fine cracks caused by shrinkage of Al₂O₃ shells, and (4) oxidation by diffusion of Al ions and O through Al₂O₃ film, respectively. The band-like structure on the surface was formed in the second phase.

In XRD patterns of MEPCMs after heat-treatment under Ar atmosphere, Al and Al₂O₃ were detected. SEM results show that the dendritic nanostructure of Al₂O₃ with arm spacing of several tens nm on the sample

surface-treated under Ar atmosphere. The weight change during heat-oxidation treatment under Ar atmosphere is divided into 2 phases: (1) weight decrease from starting weight to 89.32% just before melting point, (2) gradual weight increase to 90.60% at the end of the thermal treatment. These phenomena are (1) dehydration of AlOOH and Al(OH)_3 , (2) Oxidation of Al at cracks in Shell caused by shrinkage of Al_2O_3 or volume expansion of Al inside the MEPCM.

There was a significant difference in surface morphology between the samples thermal treated in O_2 and Ar atmosphere. Up to the third phase of oxidation under O_2 atmosphere, boehmite is dehydrated to form Al_2O_3 with volume reduction, and the shell is cleaved with the shrinkage of Al_2O_3 . Simultaneously, the crack is repaired by the oxidation of Al inside the MEPCM exposed to O_2 . In the fourth phase of oxidation under O_2 atmosphere, Al is entirely covered by Al_2O_3 ; however, Al_2O_3 continues to grow by diffusion of oxygen and Al ions through the Al_2O_3 shell. In contrast, the samples thermal treated in an Ar atmosphere does not occur crack repair and Al_2O_3 growth. Therefore, Al_2O_3 formed by dehydration of boehmite is porous. Also, since Al_2O_3 shrinks as the temperature increases, extremely fine Al_2O_3 is formed on the sample surface heat-treated in an Ar atmosphere. Small Al_2O_3 crystals formed from boehmite became finer because of Al_2O_3 crystals formed from the more significant Al(OH)_3 absorbed oxygen by Ostwald ripening. Dendritic nanostructures were formed on the surface of the samples treated in Ar atmosphere. Thus, the structure and amount of Al_2O_3 in the formed shell correspond to the amount of O_2 in the heat treatment atmosphere.

CONCLUSION: Heat-oxidation was carried out under the O_2 and Ar atmosphere to clarify the shell's forming mechanism during MEPCM synthesis. Under O_2 atmosphere, boehmite-derived Al_2O_3 grew to form dense oxide films. In contrast, under Ar atmosphere, boehmite-derived Al_2O_3 could not grow sufficiently, and finally, dendritic Al_2O_3 with many gaps was formed. It was confirmed that the higher amount of O_2 in the heat-oxidation atmosphere, the more significant Al_2O_3 shell structure formed.

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ONSET OF NATURAL CONVECTION DURING PCM MELTING

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Natural convection plays an important role during the melting process of phase change materials (PCMs). However, numerous questions still haven't been studied and answered related to this process, for example: when is the transition between conduction heat transfer to natural convection heat transfer happening in the early stage of the melting process? What conditions/properties influence this onset of natural convection? Is it possible to develop correlations pointing to the onset of natural convection?

This paper will present work will present experimental work performed in a cylindrical geometry looking specifically at the onset of natural convection for two different PCMs: n-octadecane and dodecanoic acid. A see-through cylindrical enclosure was designed and built, using a central pipe as a heat source for the melting study. Three different pipe outside diameters were used to study its geometrical impact on the onset of natural convection. Experimentally, up to five different heat source temperatures (maintained through a circulation water bath) and four initial temperatures were used. This was done to look at the impact of initial subcooling and the strength of temperature gradients in the PCM on the onset.

Results were obtained visually using webcams to capture the shape of the melting front over time. The onset of natural convection was determine by a change in shape of the melting front from concentric to non-concentric (onset of convection resulting in faster melting in the upper portion of the PCM).

Analyzing all the results and data obtained lead to important conclusions about the impact of the geometry, the initial and heating temperature, and the properties of the PCM on the onset of natural convection. For example, less melted PCM is needed for the onset of natural convection as the heating temperature is increased. The thickness of the melted PCM layer needed for onset also increases when an increase of the heating pipe diameter.

Through dimensional analysis, good correlations were also obtained to help predict the needed volume of melted PCM (or thickness of melted PCM) for onset to start. These correlations use the Gr (or Ra) and various Ste numbers can be used, at the very least, in this cylindrical geometry, to determine how much melted PCM will be needed before onset starts.

Apart from shedding light on this important part of the melting process in PCM, results from this work, through the correlations, will play an important role to help determine when studies (especially numerical) could neglect natural convection, or should account for it.

CHARACTERIZATION OF TWO PHASE CHANGE MATERIALS FOR DOMESTIC HOT WATER APPLICATION

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INTRODUCTION: The choice of a phase change material (PCM) for an application is often tricky. Several parameters have to be taken into account. The first parameter that is important in latent thermal energy storage (LHTES) is the phase change temperature. This should correspond to the temperature where the application requires the greatest energy stored or the largest amount of energy release.

MATERIALS AND METHODS: The materials used in real applications are almost exclusively non-pure materials, which implies melting or solidification over more or less wide temperature ranges. In addition, some PCMs present supercooled phenomena. It should be added that the thermal behavior of these materials in melting is very often different from the one in solidification, leading to different storage or release times.

Since LHTES work over extended temperature ranges, the amount of sensible energy involved should also be considered.

The proposed work consists to compare two PCM in terms of energy storage. The targeted phase change temperature is therefore close to 60 °C. In this study, the two selected PCMs suitable for domestic hot water (DHW) storage are RT58, a paraffin manufactured by Rubtitherm, and PEG6000, a polymer widely used in the medical and cosmetic sectors. Using a fluxmetric experimental device, the measurements and methods are presented. The heat fluxes, temperatures curves and energy balances of the two materials are plotted simultaneously in order to show the characteristics of each one and to provide input for the selection of the most suitable candidate for the considered application. The issue of cost and ageing is not addressed here but was considered before selecting the two PCMs studied.

EXPERIMENTAL PROCESS AND RESULTS: For these experiments, a fluxmetric bench is used. It makes it possible to apply temperature ramps on a sample by means of two exchanger plates heated or cooled by a refrigerated / heating circulator. These circulators are controlled by a computer in order to apply the desired thermal stress on the sample. This Fluxmetric Bench was already presented in previous works in [1,2]. The test sample consists of a parallelepiped-shaped PMMA container (21x14x1.8 cm³) into which the PCM is introduced in a liquid state in order to completely fill the container. The thickness of PMMA is 4mm. The volume of PCM inside the PPMA brick is 267 cm³. On each face of the parallelepiped, a tangential gradient heat fluxmeter is placed. Around the container a thermal insulation is placed in order to limit lateral transfers because the exchanger plates heat or cool through the largest sides of the container (21x14 cm²). The accuracy of the measurements and more details of the experimental bench are available in [2]. The sum of the heat fluxes measured every 10 seconds at each data acquisition makes it possible to estimate the quantity of energy stored (heating) or released (cooling) during the tests by the sample. The containers filled with RT 58 and PEG 6000 are heated and cooled between 20 and 70 ° C to apply on them melting and solidification cycles.

The comparative experimental test highlights the different thermal behavior of PCMs during melting and cooling processes. The melting is progressive whereas the solidification occurs abruptly. The solidification occurs earlier for RT 58 than for PEG 6000. The temperature of solidification of RT 58 is below 60°C. The RT

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58 which is a paraffin does not show any supercooling phenomenon. This is not the case for PEG 6000, which reveals a degree of supercooling of about 10 °C. In both cases, as the phenomenon of solidification occurs suddenly, the flow increases very quickly, a sign that the energy released is important. This is more significant for the PEG 6000 and the energy release time is also shorter. This is a good thing for the DHW application because the energy can be quickly available when the domestic water is drawn off. The integral of the fluxes reports the energy available between 20 °C and 70 °C. The direct comparison provides information on which MCP stores the most energy in this temperature range and this for the same volume. The PEG 6000 stores 15% more energy than the RT 58 within this temperature range.

CONCLUSION: This sort of experimental makes possible a direct comparison of energy storage between PCMs for a given range of temperature. It allows also to compare the thermal behavior of the PCMs during the melting and the solidification processes and to highlight eventually supercooling phenomena. This comparison is not easy by calculation from thermophysical properties of PCM due to the thermal properties changes during melting and solidification processes as well as density. The mass of PCM used for the experiments are closer to the conditions of real-scale applications unlike the DSC tests where the PCM sample weighs only few mg. The curves of fluxes allow also the characterization of thermal properties of PCM by inverse and optimization methods in order to provide reliable numerical models which make it possible to represent the thermal behavior of PCM [2,3].

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SYNTHESIS OF MICROCAPSULATED OF PCMS WITH NATURAL SHELL MATERIALS PREPARED ACCORDING TO GREEN CHEMISTRY PRINCIPLES

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INTRODUCTION: The only alternatives to fossil fuels are natural and renewable energy sources. Research on thermal energy storage (TES) systems that will allow continuous use of these sources have been the common subject of many scientists in recent studies. Different TES techniques are used for energy storage depending on the purpose and operation conditions. The most commonly used TES method is sensible heat storage. The other two methods of TES are latent heat storage and thermo chemical storage, which provide higher storage capacities. Latent heat storage technique that rely of phase change materials (PCM) is used for applications like heating, cooling, waste heat management and temperature control[1]. Sustainability of TES materials is becoming more important than ever with the recent “Green Deal” plan of EU. New phase change materials (PCM) developed with this perspective can offer promising solutions in various applications. The critical factors in developing such PCMs are reliability, affordability and environmentally friendliness. “Green Chemistry” principles [2] that are based on producing less waste, using less energy, natural and recyclable materials can be applied for more sustainable PCM production. The materials used at each stage of production should be selected from those found in nature, priority should be given to recycling materials, and processes should be done at lower temperatures and shorter time. There are very few studies on TES development that considered green chemistry principles into account [3]. In this study, we attempt to introduce two new microencapsulated PCMs (mPCM) developed using the principles of green chemistry. We are particularly focusing on using shell materials found in nature instead of the most polymer shells, which rely on raw materials from fossil fuels. The new mPCMs can be candidates for use in solar and electronics cooling applications.

MATERIALS AND METHODS: Two different microencapsulated PCMs were prepared using shell materials calcium borate (CaB_4O_7) and calcium carbonate (CaCO_3). Both of these materials can be found in abundance as natural minerals. As the core material (PCM) paraffin with melting point of 42-44 °C was used with CaB_4O_7 shell and lauric acid (LA) with melting point of 43 °C was used with CaCO_3 shell. The mPCMs were prepared using self-assembly method [4]. Heating cooling curves, Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) were used to characterize the new PCMs.

Results and Discussion: The heating and cooling curves between 15 °C to 60 °C of the synthesized mPCM and PCM are carried out to determine phase change performance. For both of the mPCMs phase change occurred without any super cooling. The melting and freezing occurred at similar values as well without any hysteresis. But, the expected phase change occurred at lower values than expected and was observed at 37 °C for LA@CaCO_3 and at 36 °C for $\text{paraffin@CaB}_4\text{O}_7$.

DSC analysis for LA@CaCO_3 shows that melting point and enthalpy are 45.0 °C and 34.7 J/g and freezing point and enthalpy are 36.0 °C and 36.5 J/g. For $\text{paraffin@CaB}_4\text{O}_7$, melting point and enthalpy are 38.4 °C and 71.3 J/g and freezing point and enthalpy are 42.8 °C and 75.3 J/g according to DSC results. The melting and freezing points are not symmetrical for both mPCMs unlike heating and cooling curves. This behavior is expected in DSC analysis with mg sized samples.

FTIR analysis was done to determine the success of the microencapsulation process. The analysis was run for core and shell materials as well as mPCMs to detect the existence of characteristic peaks. For both of

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the mPCMs the expected characteristic peaks were observed at a lower intensity. The results confirm that microencapsulation was achieved without any change in chemical structures.

SEM images were taken to determine the morphology and dimensions of mPCMs. For paraffin@CaB₄O₇, SEM images showed that mPCMs are uniformly distributed with compact surface, spheroid shapes and diameters of about about 150 nm diameter. For LA@CaCO₃, the SEM results show that CaCO₃ microcapsules with LA show a homogeneous distribution.

These results show that the new mPCMs with natural shell materials are promising candidates that can be used in solar and electronic cooling applications.

CONCLUSIONS: In this study new paraffin@CaB₄O₇ and LA@CaCO₃ synthesized as mPCMs based on green chemistry principles are presented. The mPCMs were synthesized successfully as shown by FTIR and SEM results. Thermal energy storage capacities can be further improved by using different shell:core ratios. The first results show that mPCMs can be promising candidates for TES applications that require melting points in the range of 42-44 °C. Further research on increasing thermal storage capacity and thermal cycling are on-going.

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THERMAL CONTACT RESISTANCE: IMPLICATIONS FOR THERMAL ENERGY STORAGE SYSTEMS

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INTRODUCTION: In thermal energy storage systems a major characteristic for charge and discharge rates is the overall thermal resistance between heat sink and heat source. Precise knowledge about thermal resistance is necessary for designing and simulating storage components. However, the thermal resistance is often simplified to bulk resistance of the materials whereas the thermal contact resistance at their interface is neglected. In this study we determine thermal contact resistances relevant to thermal energy storage systems and operating conditions. It is shown that the thermal contact resistance can have a clear effect on overall heat in- and output depending on the design of the storage component.

MATERIALS AND METHODS: Thermal contact resistances between storage material and container material were determined via a modified stationary cylinder method. The examined storage material was the metallic Phase Change Material Al-12wt%.Si and the examined container material was the Ceramic Matrix Composite C/C-SiC. The thermal contact resistance dependence on temperature (25 - 300 °C) and pressure (0 - 4 MPa) was found.

RESULTS: The thermal contact resistance between storage and container material was found to decrease asymptotically with increasing temperature and increasing pressure. For pressures over 3 MPa the contact resistance was reduced to under 1 cm²K/W.

CONCLUSION: It is concluded that thermal contact resistance can have a major effect on charge and discharge rates, especially for storage designs where several layers of materials lie between heat source and heat sink. Storage designs that take advantage of pressure between storage material and heat transport components due to solidification or thermal expansion/contraction could improve functionality. Thus, thermal contact resistance is recommended to be considered in the design of thermal energy storage systems.

DEVELOPMENT OF A PROTOTYPE TO RESEARCH ON XYLITOL CRYSTALLIZATION BY SHEARING AND SEEDING FOR ITS USE AS A PHASE CHANGE MATERIAL

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INTRODUCTION: As many renewable energy sources are intermittent, demand and energy generation are not synched, which leads to the necessity of energy storage. Thermal energy storage using phase change materials could overcome this mismatching. Recently, sugar alcohols have attracted the attention of many researchers due to their high energy storage density. Nevertheless, they have two main downsides: undercooling and low crystallization rates. In this work, seeding and shearing are proposed as means to trigger and accelerate crystallization.

MATERIALS AND METHODS: Xylitol of 99% purity from Sigma Aldrich was researched and xylitol seeds with a diameter between 315 and 400 μm were obtained from the xylitol chunks by sieving. Shear experiments were performed using an AR-G2 rheometer from TA Instruments, as viscosity was used to measure the crystallization of the sample. Three different undercooling temperatures and shear rates were performed, while the evolution of viscosity over time was measured. A crystal jacketed reactor was used to complement the results from the rheometer. Its capacity is two liters. Two Pt100 are attached, and an IKA Eurostar 60 control with a propeller stirrer is used to induce shear on the molten xylitol.

RESULTS: Shear can trigger crystallization at low undercoolings if a seed is present. Secondary nucleation is the principal force involved. The combined technique of seeding and shearing appears to be very efficient to trigger and accelerate the xylitol crystallization with an average improvement of the crystallization time by a factor of 20 compared to the one obtained in conditions of no shear. However, results are not reproducible, as the size distribution of seeds fragments were different between measurements. Using a bigger xylitol sample and multiple seeds can solve this problem, so the crystal reactor was designed and used.

CONCLUSION: Xylitol can be a suitable PCM for thermal storage application, but its low crystallization rate is a handicap that must be overcome. Rheological measurements have shown a significant improvement of the crystallization rate when the combined technique of seeding and shearing is adopted. However, results were not reproducible, which proves the necessity of larger scale experiments and therefore the design of a bigger prototype.

POSSIBILITIES AND LIMITATIONS OF PCM DEVELOPMENT USING PHASE DIAGRAMS

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INTRODUCTION: Latent heat storage using phase change materials (PCM) provides thermal energy storage systems with high storage capacities in small temperature ranges. However, there is a lack of thermally cycling stable and cost-effective PCM in certain application-relevant temperature ranges. Since most pure materials have been tested as PCM, mixtures of PCM are being investigated. In this context, phase diagrams are used to identify interesting mixture compositions (e.g. eutectics). Phase diagrams can be determined experimentally or calculated using thermodynamic models. Both measurements and calculations are subject to uncertainties regarding the determined temperature and composition of an interesting mixture. In this work, these uncertainties are discussed for phase diagrams of salt hydrate mixtures. The discussion is based on results from own research projects and on published work from literature.

MATERIALS AND METHODS: In the project properPCM, solid-liquid phase diagrams of mixtures of salt hydrates were calculated with the modified BET model. To check the phase diagrams, predicted eutectic compositions were experimentally tested via DSC and calculated enthalpy-temperature curves of salt hydrate mixtures were compared with DSC results. Additional experimental methods, e.g. the DSC three-step method and a so-called eutectic device, can be applied to increase the prediction accuracy of a eutectic composition. In addition to results from own projects, a literature survey concerning the state-of-art of PCM development using solid-liquid phase diagrams of salt hydrates is conducted.

RESULTS: The accuracy with which the exact composition of a eutectic mixture can be determined is limited by several uncertainties. First, the temperature and composition uncertainties of predicted phase diagrams being a consequence of the uncertainties of the available experimental data that is required to determine the necessary model parameters. Second, the uncertainties of experimental techniques to analyze the composition of investigated samples (e.g. titration methods). Third, the uncertainties of measured or calculated enthalpy-temperature curves. According to the current state of literature, these uncertainties are often neither determined nor adequately taken into account.

CONCLUSIONS: Phase diagrams are an effective tool to identify eutectic mixtures. Careful experimental verification is crucial to verify and eventually optimize the predicted eutectic composition. Thermal cycling stability measurements under application conditions can confirm that the identified eutectic mixture can be used as a PCM despite the remaining uncertainties regarding its exact composition.

SHAPE-STABILIZED PHASE CHANGE MATERIALS OBTAINED BY SINGLE SCREW EXTRUDER FOR BUILDING APPLICATIONS: THERMO-PHYSICAL CHARACTERIZATION

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INTRODUCTION: Extrusion is one of the most conventional technologies used to manufacture polymers and this study use this equipment to produce the formulation previously optimized. If one formula can be extruded in the single screw extruder means that the process is easily scalable. This study aims to show the results of four polymer-based PCM manufactured by a single screw extruder, at the University of Birmingham, and their thermos-physical characterization, performed at the University of Barcelona.

MATERIAL DEVELOPMENT AND CHARACTERIZATION: The formulations in this study were manufactured by a single-screw continuous-extrusion device (Brabender GmbH, Germany). The extruder can work up to 450 °C and achieve rpm from 0.2 to 350. The extrusion conditions are the following listed in Table 1.

Table 1. Extrusion conditions followed to develop the formulations under study.

Temperature (°C)	140-150 °C
Rotating speed	2-10 rpm
Die Round die	4mm diameter
Cooling bath	250 °C

Four formulations have been manufactured in this study and the composition in weight percentage is described in Table 2. HDPE was from HDPE was of Total XSene 55060 (Total Petrochemicals, France).

Table 2. Formulations manufactured by single screw extruder at the Birmingham Centre for Energy Storage

	HDPE (wt.%)	PCM (wt.%)	Magnesite (wt.%)
HDPE 100	-	-	-
HDPE 10% PCM 10%	90	10	-
HDPE 10%PCM 10% M 20%	70	10	20
HDPE 10%PCM 20% M 20%	60	20	20

A thermal cycling test was used to assess the thermal reliability of the materials formulated. The test was performed inside a BIOER thermal cyler. 1000 thermal cycles were performed between 15 °C and 45 °C using 5 °C /min heating rate with an isothermal step at 45 °C and 15 °C for 3 minutes for building applications. The samples were characterized by DSC and Fourier-Transform Infrared spectroscopy (FT-IR) before and after the thermal cycling test to check the thermal and chemical stability. The thermophysical properties of the materials under study were analysed using differential scanning calorimetry (DSC). The equipment used to perform the measurements was a DSC 822e Star3+ from Mettler Toledo. The amount of sample per measurement was around 15 mg inside a 40µL aluminium crucible. The measurements were done under 50 mL/min N2 flow and 0.5 °C /min heating rate. The Fourier-Transform Infrared spectroscopy (FT-IR) to evaluate the degradation of the samples before and after the thermocycling test was a Spectrum Two™ from Perkin Elmer supported by Dynascan™ interferometer and OpticsGuard™. The thermal stability and degradation behaviour of the samples under study was performed by thermogravimetric analysis. The Thermogravimetric Analyzer (TGA) used was from TA Instrument (SDTQ600). The tests were carried out under 50 ml/min airflow, from 150 °C to 500 °C with a heating rate of 10 °C/min.

RESULTS: Chemical stability FT-IR results are shown in Figure 1. These results show the four samples under study FT-IR spectra before and after the thermal cycling test and no significant differences can be seen. Therefore, the polymer-based PCMs are chemically stable under the cycled conditions.

Figure 1. 4 polymer-based PCMs FT-IR spectra obtained before and after the thermal cycling test

The thermophysical properties of the four samples formulated in this study were analysed before and after being cycled and the results are shown in Figure 2 (a). The sample containing PCM without flame retardant (magnesite) can maintain its thermal storage capacity after 1000 cycles. However, when magnesite is added to the formulation, the latent heat storage capacity is reduced. The phase change temperature remains constant over thermal cycles and is almost the same between samples developed in this study. Figure 2 (a) shows the melting enthalpy (J/g) and the melting temperature ($^{\circ}\text{C}$) of the samples under study, before and after thermal cycling. Finally, the thermal stability was tested by TGA and the results are shown in Figure 2 (b). The samples without magnesite present a similar profile, in the same way, the samples with magnesite have a similar one. The decomposition follows several steps which are in accordance with their compositions. The maximum working temperature of the samples containing PCM is around 310°C while it is 335°C for the HDPE without PCM.

Figure 2. (a) DSC results obtained for the 3 polymer-based PCMs developed in this study before and after the thermal cycling test. (b) TGA results obtained for the 3 polymer-based PCMs and the HDPE developed in this study before and after the thermal cycling test

CONCLUSIONS: Four shape-stabilized PCM formulations were developed using a single screw extruder. These SSPCMs are polymer-based PCMs. The formulations include microencapsulated PCM and magnesite as a flame retardant. The thermal and chemical stability of the samples was analysed before and after 1000 thermal cycles. The chemical stability is demonstrated by the FT-IR and TGA results obtained. TGA results show similar maximum working temperatures (around 310°C) for the samples with and without PCM. However, the DSC results showed that there are some changes in their thermal storage capacity when magnesite is included that could be an interaction between the magnesite and the MPCM. Further investigation needs to be done to understand the reasons and propose solutions. Further, research is required in terms of flammability and mechanical properties to assess their applicability in buildings. Flammability will be studied by epiradiator and limit oxygen index tests and mechanical properties will be studied by dynamic-mechanical analysis.

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SENSITIVITY ANALYSIS OF EXAMINATION METHODS TO DETERMINE THE DEGRADATION OF ERYTHRITOL AND HD-PE

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Energy storage systems are an important topic for reducing discrepancies between energy supply and demand. Latent heat storage systems can be used for thermal energy storage. The materials used in these storages are so-called phase change materials (PCM), which have been the subject of research for years. Especially in cases of PCMs for process heat applications organic materials underlie often a significant degradation. Degradation of individual PCM has already been investigated in many cases, but so far there have been only a few investigations on procedures for accelerated aging tests and analysis methods to determine degradation parameters of PCMs. Typically time consuming cycling procedures are used, as for example described in the guidelines of RAL GZ 896. Analysis of degradation is most often done using calorimetric measurements. Within the framework of the project PCM Metro II, funded by the BMWi, different classes of materials will be investigated with the aim of establishing a quick but also precise standardized method for accelerated aging of new materials depending on the class of material.

Two materials for process heat applications, Erythritol and High Density Polyethylene (HD-PE), have been investigated, where a sensitivity analysis of the degradation was performed. The material samples were aged at three temperature levels 10, 20 and 30 Kelvin above the melting point for 5, 25, 50, 250, 500 and 1000 hours. For this purpose, the samples were filled into laboratory bottles in solid state and sealed with a lid. Five samples per time and temperature step were prepared and characterized by different analytical methods after aging. Thermal analyses such as differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) are used, but also gravimetric analyses and optical methods such as Fourier Transform infrared spectroscopy (FTIR), UV-Vis spectroscopy, color change measurements and Raman spectroscopy are applied. The aim of these analyses is to find out which analysis method is the most sensitive to detect a change in the material and also to estimate changes over time.

The DSC analysis of Erythritol shows a maximum decrease of melting enthalpy of 9 % at an ageing temperature of 10 Kelvin above the melting point after 1000 hours. A complete analysis of the samples, which were aged 20 and 30 Kelvin above the melting point, was not possible with the DSC, because a different crystal structure is formed during the measurements, which makes a comparability of the results impossible. In the TGA, the Erythritol samples with the highest ageing temperature show a multi-stage degradation of the material from an ageing time of 250 h, which is single-stage in the pure sample. This shows that a chemical change occurs in the sample. The two thermal analyses are still pending for HD-PE. Both Erythritol and HD-PE show a change in color after aging. However, this change does not occur equally in both materials. While Erythritol shows a uniform discoloration of the overall material, HD-PE shows a stratification of the color, which is related to the higher viscosity of the material. Nevertheless, the following applies to both materials: the higher the ageing temperature and the longer the ageing process, the darker the material becomes. Based on the phenomenon of color change, it can be assumed that optical methods will prove to be suitable tools for evaluating the discoloration. FTIR and Raman can be used to investigate whether the discoloration is accompanied by a chemical change in the material. In the case of Erythritol, both methods of analysis show changes that still need to be examined in detail. For HDPE these analyses are still pending.

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Short oral lectures/posters

The gravimetric analyses of both materials have shown that the changes in mass in relation to the total mass are very small (less than 1%), so that this analyzing method is not useful to evaluate the degradation of the materials.

In summary, the work shows that different analytical methods are suitable for determining temperature depending aging of HDPE und Erythritol, but the sensitivity of the individual analytical methods has yet to be evaluated.

DEVELOPING PCM-PVA GEL COMPOSITE BIO-INSPIRED BY WHALE BLUBBER FOR TES

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INTRODUCTION: The energy demand of the world is increasing day by day. Current fossil fuel based energy systems are non-renewable and cause climate change threatening the future of the world. Thermal Energy Storage Systems (TES) is one of the key technologies that allow to use renewables efficiently. TES is performed based on three kind of methods: sensible, latent and chemical. The latent heat storage can be done using Phase-Change Materials (PCM). Developing sustainable PCMs is vital to extend its use in various TES applications. The aim of this study is to develop novel bio-inspired PCM composites similar to ones used in living organisms in nature. For instance, warm-blooded species want to keep their body temperature constant at around 37°C – can vary depending on the species – so that their vital organs and metabolisms can function properly. For example, whales have a special structure of adipose tissue called "blubber" to achieve this¹. Hydrogels have a porous structure that includes water molecules in the matrix. Such gels can cool spontaneously by evaporation of water in their structure. With this property they are used as heat sinks¹. In this study, new composite with poly vinyl alcohol (PVA) gels and PCMs similar in composition to blubber is investigated.

MATERIALS AND METHODS: PCM was developed based on some mixtures of fatty acids found in whale 'blubber'. The mixture consisted of oleic acid, palmitic acid, stearic acid, myristic acid and oleyl alcohol. Composites of the developed PCMs were prepared with PVA gel, which a hydrogel with porous structure. The method used in the preparation was as follows: The PCM mixture consisting of 51% oleic acid, 16% palmitic acid, 6.7% stearic acid, 5.8% myristic acid and 20% oleyl alcohol was mixed with magnetic stirrer for 2 hours at 70°C. First PVA in powder form was dissolved in pure water, then PCMs at desired amount was added into this solution and mixed at 90°C for 2 hours. This mixture was poured into a rectangular mold with a thickness of 8.5 mm. The molds were kept at -18°C for 14 h and then for 10 h at room temperature. This freeze-thaw process was repeated 6 times¹. Physical (SEM and leakage) and thermal (DSC and heating-cooling curve) characterization of the composite were done and all results were compared to pure gel to determine thermal performance of the developed PCM-PVA gel composite.

RESULTS AND DISCUSSION: Heating-cooling curves measured between 5 – 45 °C shows that, melting point of PCM is about 37°C and the freezing point is about 27°C. There is a supercooling of about 10°C, which is expected for most fatty acids. The melting point for the fatty acid was similar to the whale blubber mixture, which was the bio-inspiration here. For the PCM-PVAgel composite supercooling is not seen. This shows PVA gel was effective in decreasing supercooling.

The melting and freezing points of PCM determined by DSC were 35,2°C and 27,99°C, respectively. These results are consistent with the heating and cooling curve. The latent heats of PCM during melting was 16,1 J/g, and it was 16,4 J/g for freezing.

PVA and PCM-PVA composite samples were analyzed by SEM to determine the porous structure. The pore size of PVA was about 1µm. The SEM images for PCM-PVA gel samples show that pore sizes were enlarged by at least 10 fold reaching to diameters in the range of 10 – 50 µm. This shows PCM has filled in the pore structure of PVA.

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PCM and PCM-PVA composite structures were heated in an incubator at 50°C for 1 hour. Then it was checked if there was any leakage at room temperature. According to the analysis, it was observed that the gel structure was leak-proof up to 50°C.

CONCLUSION: A PCM mixture bio-inspired by whale blubber was developed. The composite of PCM with PVA gel was prepared to have a form stable and leak-proof product. The SEM results show that PCM was trapped in the porous matrix of PVA and no leakage observed. Latent heats of PCMs determined by DSC need to be further improved. However, DSC analysis may not give accurate latent heat values for such multi component mixtures. Thermal energy storage potential of PCM-PVA gel composite including self-evaporating property of PVA and latent heat of PCM has to be determined in an experimental set-up. The PCM-PVA gel composite is suitable to be prepared in thin layers and can be used in applications requiring temperatures around 37 °C. In further studies, different percentages of PCM will be added to the PVA gel and will be tested in the experimental TES set-up under development.

KEYWORDS: TES, Bio-inspired, blubber, PCM, PVA

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REDUCTION OF ROTATION PHASE SUPERCOOLING IN NANO N-DOCOSANOL PHASE CHANGE SLURRIES

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INTRODUCTION: Phase Change Slurries (PCS) are an efficient medium for isothermal energy storage and transportation. In nanometer-sized dispersion droplets, supercooling decreases the available heat capacity in a specific temperature range due to a shift in the phase change temperatures. Since PCM are mostly used in applications with narrow operating temperature interval, supercooling can lead to unusability of PCS.

MATERIALS AND METHODS: Differential Scanning Calorimetry (DSC) is used in combination with X-ray diffraction (XRD) to characterize the PCS prepared by ultrasonication.

RESULTS: We confirm that n-docosanol exhibits similar rotation phases as previously observed in linear alkanes. Also, the increasing melting temperature by addition of water was reproduced. With decreasing particle size, the phase transitions diverge to lower temperatures. Upon addition of nucleation agents, the degree of supercooling could be reduced significantly for some phases.

CONCLUSION: A model for the n-docosanol crystallization is developed, which helps to understand supercooled rotation phases and simplifies the transfer to other organic PCS.

STABILITY OF LATENT HEAT STORAGE UNITS: EVALUATION BASED ON THE COMPATIBILITY TESTS

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INTRODUCTION: The European Green Deal issued in 2019 introduced the strategy towards the prosperous society with circular economy and no net emissions of greenhouse gases in 2050. Buildings integrating energy from renewable energy sources (RES) for their operation are one of the ways how to mitigate CO₂ emissions. Efficient thermal energy storage may contribute to the overcoming temporal mismatch between energy generation and energy demand. Integration of latent heat thermal energy storage (LHTES) represents much more effective way for the energy storage because of the high volumetric storage density compared to sensible heat thermal energy storage (SHTES). Thus, Phase Change Materials (PCMs) suitable for LHTES were subjected to the investigation performed at Brno University of Technology. PCMs needs to be encapsulated due to their phase change from solid to liquid state. The compatibility of PCMs with container material is a key parameter for ensuring long service life of LHTES. Therefore, this study is focused on the investigation of the compatibility of two organic and two inorganic PCMs with four types of metals and three types of plastics.

MATERIALS AND METHODS: Four metals (carbon steel DC01-A-m, aluminium AW 1050 H11, copper CW024A and brass CW508L) and three plastics (PP-H, PE-HD and PVC-U) were selected as potential materials for PCM containers as they are considerably low costs and widely available in EU countries. The samples of each metal were divided into 12 sets of three. Individual samples were approximately 2.0 cm wide, 10.0 cm high and 0.1 cm (carbon steel) or 0.05 cm (other metals) thick. Each sample set of plastics (totally 64 sample sets, 16 sets per one PCM) consisted of three individual plastic plates with dimensions 10x1x0.15 cm to minimize impact of possible defective samples on the results. Four PCMs were selected for testing as representatives of PCMs applicable for improving of heat storage capacity of buildings that might be integrated in the structures. Paraffin-based Linpar 17 and Linpar 1820 from Sasol represent organic PCMs, Rubitherm SP22 and Rubitherm SP25 represent inorganic PCMs based on salt water mixtures and additives. All PCMs were analysed by Different Scanning Calorimeter (DSC). The amount of latent heat of the selected PCMs varies between 122 and 152 J·g⁻¹ and peak temperature between 22 and 28 °C. The test beakers with samples immersed in PCMs were placed into peltier-cooled incubator and exposed to repeating temperature cycling with temperatures ranging from 15 °C to 40 °C. The duration of the test was 16 weeks for plastic samples and 12 weeks for metal samples. The evaluation procedure was based on monitoring of the mass changes and visual surface changes in the tested metal and plastic samples. Therefore, the sample sets were removed at specific intervals from the beakers with PCM to perform measurements of their mass. The gravimetric method was used to evaluate the compatibility. Percentage change in mass was calculated for every plastic sample. And for the metals, the main parameter evaluating compatibility of metal-PCM combinations in this study was corrosion rate (CR). CR is defined as a change of mass Δm relative to surface area of the metal sample in specific experimental time period.

RESULTS: Significant mass change in PP-H and PVC-U samples immersed in organic and inorganic PCMs was observed. PVC-U samples were almost inert to PCMs in all cases and measured changes were negligible compared to the other tested plastics. There was observed fast penetration of organic PCMs Linpar 17 and Linpar 1820 into PE-H and PP-HD during first four weeks. The mass change during the remaining part of the experiments was almost the same in organic PCMs. This means that the tested plastic samples were almost fully saturated by the PCMs during first four weeks of the experiment. In the end the maximum mass

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changes did not exceed 7 % in organic PCMs. On the other hand, the mass change in PE-HD and PP-H immersed in inorganic PCMs (Rubitherm SP22 and Rubitherm SP25) is significantly lower compared to organic based PCMs. Maximum mass change of 1.8 % was identified/occurred with PP-H immersed in Rubitherm SP22. Immersion in organic PCMs caused no visual changes on the surface of brass, aluminium and carbon steel samples. Local surface changes (darker stains) and tarnishing occurred on the copper samples. The extent of these changes increased with longer exposure to the PCMs. Dark brown stains appeared on the surface of copper and brass samples. Corrosion also occurred on the surface of the copper (blue corrosion) and carbon steel (dark red and brown corrosion) samples. The highest values of CR in case organic PCMs were achieved in case of carbon steel, where the CR exceeded $4.0 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{year}^{-1}$. Calculated CRs for samples immersed in inorganic PCMs gradually increase from aluminium to brass, copper and finally carbon steel. The highest values of CR were calculated for carbon steel in Rubitherm SP25 (up to $13.897 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{year}^{-1}$).

CONCLUSION: This experiment evaluated the compatibility of three types of plastics and four metals used for PCM containers with two organic (Linpar 17, Linpar 1820) and two inorganic PCMs (Rubitherm SP22, Rubitherm SP25). To identify the compatibility of materials, plastic and metal samples were immersed in the PCMs for up to 16 weeks and then weighed and mass change and the corrosion rate were calculated. Overall, mass changes of PVC-U samples in contact with all PCMs were almost negligible. The highest mass change occurred in PP-H and PE-HD samples immersed in organic PCMs. The experiment has shown that copper and carbon steel are unsuitable for long-term exposition to inorganic based PCMs because both metals displayed signs of surface corrosion and change of color at the end of the experiment. The results indicate that aluminium is the best suited for the role of PCM container as it had the lowest mass loss and CR and it suffered only minimal visual changes during the experiment.

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OWN SYNTHETIZE NANO-ENHANCED FATTY ACID PHASE CHANGE MATERIALS (NEPCM): A COMPARISON OF PROPERTIES

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INTRODUCTION: Thermal comfort in the building sector is a crucial issue when selecting the materials to make the building envelope as well as the system to climatize the indoor temperature and humidity. However, these important decisions will deal also with the energy efficiency of the building. At this moment, more than 40% of total energy consumption worldwide is spent by domestic and commercial buildings (hospitals, commercial centres, libraries, schools, etc.) [1,2]. Passive thermal energy storage solutions are being the clue to improve the thermal efficiency by thermal regulating and controlling the indoors conditions [3]. Phase change materials (PCMs) are those materials with better characteristics [4]. This compromise makes PCMs very attractive to be implemented as passive systems in building envelopes with the purpose of energy efficiency improvement. Thereby, to improve thermal conductivity (k) of organic PCMs is mandatory to modify the composition of the PCMs. This work aims to improve this property (k) by adding low percentages of nanoparticles and characterize their properties in the liquid state. The results presented in this paper are the achievements obtained in DIOPMA research group developing nano-enhanced (NEPCMs).

MATERIALS AND METHODS: The owns synthesized NEPCMs developed by researchers at University of Barcelona, were capric acid (CA), palmitic acid (PA) and a eutectic mixture of capric and myristic acid, 75/25 respectively (CA-MA). Capric acid and palmitic acid samples were doped with CuO nanoparticles from 1 to 2 wt.%. However, capric acid and the eutectic mixture were doped with SiO₂ nanoparticles from 0.5 to 1.5wt. All samples had a percentage increment of 0.5wt. The results obtained for the SiO₂ NEPCM have been published by Martin et al. [6] and the results obtained for the CuO have been published by Barreneche et al. [7]. The samples under study were observed by scanning electron microscope (SEM) Quanta 500. Thermophysical characterization was performed by differential scanning calorimetry (DSC). The thermal conductivity was measured using a K2PRO hot wire at liquid state.

RESULTS: The main results obtained are summarized in this section. SEM images show the picture of the developed nano-enhanced PCMs. Thermal conductivity results show an enhancement in thermal conductivity in all samples. For all samples, the higher nanoparticles content, the higher the thermal conductivity. Also, thermal conductivity obtained with SiO₂ NEPCM is higher than the one obtained for CuO NEPCM. This is due to the interaction between the CuO and the base PCM due to the dispersant agent added to obtain the CuO nanoparticles. Regarding the initial conductivity of the fatty acids, which were 0.143 W/m·K for CA, 0.145 W/m·K for PA and 0.180 W/m·K for CA-MA samples, the CuO nanoparticles granted an enhancement in thermal conductivity for CA and PA fatty acids respectively of: 13.29% and 23.45% with 0.5wt.%, 26.57% and 42.76% with 1wt.%, 46.85% and 53.79% with 1.5wt.%, and 64.34% and 58.62% with 2wt.% of CuO nanoparticles. Whereas SiO₂ nanoparticles showed a more significant increment for CA and CA-MA respectively of: 179.72% and 33.33% with 0.5wt.%, 242.66% and 66.67% with 1wt.% and 291.61% and 122.22% with 1.5wt of SiO₂ nanoparticles.

The DSC results of the nanofluids under study shows higher melting enthalpy than those nanofluids developed with SiO₂ nanoparticles. Regarding the initial values of melting enthalpy of CA, 154 KJ/mol; PA, 186 KJ/mol and the eutectic mixture of CA-MA, 153 KJ/mol; CuO nanoparticles gives an increment of 19%,

ENERSTOCK 2021

Short oral lectures/posters

11% and 3% for CA and 9%, 3% and 3% for PA with 1wt.%, 1.5wt.% and 2wt.% of nanoparticles respectively. Whereas SiO₂ nanoparticles, brings and enhancement of 4%, 7% and 9% for CA and 1%, 3% and 3% for CA-MA samples with 0.5wt.%, 1.5wt.% and 2wt.% respectively.

CONCLUSIONS: Several NEPCM have been developed and optimized. SEM images showed that nanoparticles dispersion is achieved. Thermal conductivity of the samples increase with the addition of nanoparticles. Besides, the thermal conductivity increments are higher for the NEPCM containing SiO₂ nanoparticles. The maximum thermophysical properties values seems to be for the samples containing 1wt.%. On the other hand, melting enthalpy results reveals a higher increment in CuO samples with a maximum value of 19% with 1wt.% for CA samples.

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MEASURING CRYSTALLISATION RATES OF PHASE CHANGE MATERIALS AS A FUNCTION OF SUPERCOOLING

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INTRODUCTION: In contrast to phase change materials (PCM) characteristics like melting temperature, heat of fusion and even cycling stability, data on crystallisation rates as a function of supercooling are rarely found in literature. Though, slow crystallization kinetics at typical small supercooling in thermal energy storages limit the usability of certain PCMs. In these cases, even if nucleation is successful, the growth rates of the crystals is too low for getting sufficient heat output. Problems arise not only with sugar alcohols, but also with some binary or ternary eutectics of salt hydrates.

MATERIALS AND METHODS: A broad screening of PCMs of different material classes shall be carried out. As crystallisation properties are known to get worse with increasing number of components, binary and ternary eutectics are investigated for PCM with good crystallisation kinetics, such as salt hydrates, alkanes and fatty acids. In a first step, crystallisation rates were determined for novel eutectic PCMs based on salt hydrates, that were successfully calculated with the BET-model and experimentally verified within the project properPCM. Both PCMs with known bad crystallisation properties (e.g. sugar alcohols) and eutectics of fatty acids and fatty acid methyl esters will be examined shortly.

A method was developed to determine crystallisation rates with a transmitted light polarized microscope and integrated heating stage and camera. Since most PCMs that were analysed supercool without nucleating agent significantly, the crystallised sample on the microscope slide was only melted partially by placing a heating wire on the cover glass. After switching off the voltage at the heating wire, the sample cools rapidly down to the temperature given by the heating stage. The crystal growth is measured by taking pictures at regular intervals and evaluated with the microscope software. Additionally, a measuring device with better heat dissipation from the sample is being built to investigate crystallisation rates of PCMs.

RESULTS: For both quasibinary and ternary eutectics of salt hydrates the crystal growth rates are often very low (< 0.1 cm/min) for supercoolings ΔT less than 10 K. Then a considerably rise in crystal growth is detectable until a maximum crystallisation rate is reached around $\Delta T = 30$ K to 40 K. However, only low supercoolings are essential for the usability as PCM in a heat or cold storage tank.

CONCLUSION: The characterization of PCM and especially for eutectic PCM should include measurements on the crystal growth rate as a function of supercooling. Otherwise the selected phase change material might fail in the application, because it does not crystallize during cooling or shows insufficient heat output on crystallisation.

DEVELOPMENT OF MICROENCAPSULATED PHASE CHANGE MATERIALS SUITABLE FOR FLUIDIZED BED THERMAL ENERGY STORAGE SYSTEMS

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INTRODUCTION: Finding clean and affordable energy is one of the most important problems in the world. Fossil fuels that are used widely today cause severe damage to the environment and have to be replaced by renewables as soon as possible. Renewable energy technologies must supply uninterrupted production in order to realize the transition to non-fossil fuel future. Thermal energy storage systems (TES) offer a promising method to close the gap between supply and demand of renewables. Phase changing materials (PCMs) used in latent heat TES method can be applied in various heating and cooling systems. It is very important to use components that can deliver stored heat/cold to the user efficiently. TES in packed beds are used in solar and industrial waste heat applications to provide high energy conversion (Arfaoui et al., 2017). In recent studies, fluidized beds with PCMs are used to achieve compact systems for solar thermal applications. In this case PCMs in particulate form serves both as TES and fluidized mediums (Barrientos et al., 2016). PCM with a melting point of 50°C in granular form was tested in fluidized bed and found to be stable 15 charging-discharging cycles. The challenge with PCM use in fluidized beds is to find an encapsulation that is thermally stable and durable during fluidization. The aim of this study is to develop microencapsulated PCMs suitable for fluidized bed system that can be used in solar heating applications for buildings.

MATERIALS AND METHODS: Paraffin with melting-freezing range of 42-44°C was chosen as PCM. The core material (PCM) was encapsulated with CaCO₃ as shell material using self-assembly method (Shiyu et al., 2014). Firstly, CaCl₂ was dissolved in deionized water. Nonionic and hydrophilic surfactant mixture was used to prepare water-oil emulsion of paraffin. The CaCl₂ solution was added dropwise to the paraffin and surfactants mixture. It was then mixed continuously at 1000 rpm to obtain homogeneous emulsion. Aqueous Na₂CO₃ solution was added dropwise to the paraffin emulsion as a final step (Emir et al., 2021). The inorganic shell material chosen here has higher thermal conductivity than alternative organic shell materials. The thermophysical properties of the synthesized microcapsules were characterized to determine their suitability for use in fluidized bed TES system.

RESULTS AND DISCUSSION: Properties for thermal energy storage (phase change temperature and latent heat) were determined by Differential Scanning Calorimetry (DSC). The results of DSC analysis for the synthesized paraffin@CaCO₃ microcapsules showed that melting point and enthalpy were 49.5 °C and 52.6 J/g and freezing point and enthalpy were 32.6°C and 51.5 J/g. The supercooling seen here can be explained by the small sample sizes used in DSC analysis. The phase change behavior was also analyzed with heating and cooling curve. The results showed symmetric phase change without any supercooling.

Particle size affects the fluidization behavior. SEM images were taken to determine the morphology of paraffin@CaCO₃ microcapsules. SEM results show that particles are uniformly distributed with compact surface and spheroid shapes with diameters of about 5 µm diameter.

Thermal conductivity is also an important property for heat transfer in the fluidized bed. Hot Disk Thermal Constants Analyzer was used to measure thermal conductivity of paraffin@CaCO₃ microcapsules and paraffin. The results showed that thermal conductivity of paraffin was increased by 2.8 times by encapsulating with CaCO₃ reaching to a value of 0.52 W/mK. In comparison to a polymer-coated paraffin microcapsule, which will typically have a thermal conductivity of around 0.15 W/mK, this is a significant increase. Higher thermal conductivity of particles in fluidized phase will lead to uniform temperature

ENERSTOCK 2021

Short oral lectures/posters

distribution. In addition to the advantage of thermal conductivity, using inorganic shell material avoids depleting fossil fuel based polymer materials that are harmful to the environment, costs less and shortens encapsulation reaction time.

According to these results, the synthesized microcapsule can be a candidate to be used in fluidized beds for compact TES applications. Further tests in fluidized beds need to be done to confirm suitability of the paraffin@CaCO₃ microcapsules.

CONCLUSIONS: The results showed that the paraffin@CaCO₃ microcapsule could be a promising PCM candidate for thermal energy storage systems, particularly for fluidized bed systems. More research will be conducted on increasing thermal storage capacity. The fluidization behavior and phase change performance of paraffin@CaCO₃ microcapsule should be tested in fluidized bed TES system.

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THERMAL CHARACTERIZATION OF A LATENT HEAT THERMAL ENERGY STORAGE SYSTEM THROUGH AN 8.5 kWh EXPERIMENTAL PROTOTYPE

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INTRODUCTION: the use of thermal storage systems (TES) aimed at recovering heat for better using renewable energy is a fundamental step for the efficiency, economic and environmental sustainability of energy processes. Latent heat storage systems using phase change materials (PCM) have intrinsic compactness and high storage capacity. Then, an experimental plant, called ATES devoted to the characterization of PCM for applications up to 400 °C (depending on the used heat transfer fluid), has been built at CR ENEA Casaccia in Italy. Furthermore, starting from the acquired knowledge, a prototype, called LH01, has been developed and implemented, in which some solutions have been adopted to enhance the heat exchange phenomena highlighted above. This paper treats of the experimental campaign recently carried out, using solar salts as PCM, through this equipment to deepen the heat exchange dynamics, optimize the system and make it ready for industrial applications.

MATERIALS AND METHODS: The prototype was designed for a nominal capacity of 8.5 kWh, using about 100 kg of solar salt as PCM. A stainless steel heat exchanger (length: 12 m; external diameter 16 mm) was immersed in the system, which supplies (in charge) or absorbs (in charge) the heat from a heat transfer fluid (HTF), consisting of the Paratherm NF thermal oil. A handling system was properly realized to warm or cool the HTF with a power of 21 kW. It uses a magnetic pump drive to make flowing the oil up to 1500 kg/h. Its flow was measured by a flowmeter with Coriolis effects, about 40 thermocouples were installed to collect the temperature data. A LabView interface remotely controlled completes the equipment. The TES material was subjected to thermal cycles in the range of 200-260 °C.

The following tests were essentially carried on:

- pre-heating: it consists in heating and circulating the oil from room temperature up to about 200 °C (ramp of 120 °C/h). Subsequently, this temperature is kept constant until the whole PCM reaches a uniform temperature (about 6 hours);
- full charge/discharge cycle: after the pre-heating, the oil is warmed up to 260 °C in by-pass, that means keeping the valves related with the PCM module closed for about 15 minutes; then the valves are opened and the PCM is warmed by the oil at the constant temperature of 260 °C for 12 hours; afterwards, for 15 minutes, a new by-pass circulation is carried on to cool the oil up to 200 °C and making possible the discharge step for 12 h of oil circulation in the TES at a constant temperature of 200 °C.
- thermal losses at constant temperature: it consists in the preheating and full charge at different temperatures the TES: 200 °C, 220 °C, 240 °C and 260 °C and allowing the oil circulation at constant temperature; then, through the measure of the oil flow and the inlet and outlet temperature of the storage module during the time it is possible to assess the requested loss;
- thermal losses at the inactive system: with the module fully charged at different temperatures, the system is switched off for a period. Then measuring the cooling of the oil during this time it is possible to evaluate this kind of losses;
- charge and discharge set of cycles: this is a typical charge/discharge cycle, lasting about 12 hours, in which the oil temperature is regulated as follows: from 200 to 260 °C in 1 hour; 260 °C for 5 hours; from 260 to 200 °C in 15 minutes and 200 °C for 5 hours.

RESULTS: The results showed that the maximum energy charged in the module is a function of the HTF flow rate (between 200 and 800 kg/h) and varies from 6.3 to 6.9 kWh, with times between 5 and 13.5 h. The

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average charging power is higher at high flow rates: 1.8 kW at 800 kg/h, 1.29 kW at 400 kg/h and 0.8 kW at 200 kg/h. During the discharge phase, on the other hand, the energy released by the PCM remains substantially constant (4.98 kWh) in the flow rate range 800-400 kg/h (turbulent regime), while it is lower (3.96 kWh) than 200 kg/h (laminar regime). Furthermore, by decreasing the capacity, the discharge times increase (from 6.5 to 8 h) and the discharge power decreases (from 0.49 to 0.27 kW).

As regards the thermal losses, at the same flow rate, they vary linearly with the temperature and are between 200 and 250 W at 200 °C, and between 250 and 300 W at 260 °C.

Finally, charge and discharge set of cycles leads to storage of 4.5-5 kWh in 5h for each cycle, except for the first one where, starting from a colder system, about 6.6 kWh was stored. Moreover, it was noted that, with cycles of the chosen duration, part of the charged energy is not then recovered and therefore remains within the TES.

CONCLUSIONS: The tests carried out showed high energy storage densities and excellent cycling. Nevertheless, the results obtained, although encouraging, suggest further design optimizations regarding heat exchange surfaces and reduction of thermal losses to increase the utilization factor of PCM.

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MEASURING THERMOPHYSICAL PROPERTIES FOR AN OPEN-SOURCE PCM LIBRARY

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INTRODUCTION: Thermal energy storage systems are of utmost importance to the energy turnaround, i.e. the proliferation of renewable energy sources. Thermal energy storage (TES) in form of heat can be divided into three different concepts; sensible, latent and thermochemical storage. While sensible TES are well-established and used in every household, the latent and thermochemical heat storage technology is not yet fully developed and still requires fundamental research particular with regard to long-term behavior. One of the advantages of latent storages over sensible storages are the small operational temperature differences required for short-term storage applications, i.e. day-night transfer. This leads to higher efficiency when combined with heat pumps and thus an overall decrease in energy consumption. The core of a latent storage is the phase change material (PCM), which undergoes the phase transition from solid to liquid or vice versa to release/store energy. Accordingly, the most important selection criteria of a PCM is its phase change temperature, which has to match the temperature of the application. However, there are additional criteria to be respected, such as a large phase change enthalpy. In order to have a fair and concise selection process, knowledge about the basic thermo-physical properties are essential. Here the author's show the results of a second round of measurements following such a structured methodology.

MATERIALS AND METHODS: A differential scanning calorimetry procedure has been applied to determine phase change enthalpy and onset melting temperature of each phase change material using a single set of parameters. Additionally the range of supercooling is determined for a given sample size. Thermogravimetric analysis has been employed to determine the maximum operating temperature using a method adapted from international specifications for similar purposes. Additionally the density has been measured using an oscillating u-tube. For purposes of reproducibility, each material has been measured 3 times and the mean and standard deviation has been determined.

RESULTS: Within the measurement campaign a manifold of reliable thermo-physical data has been determined for over 80 PCM, namely enthalpy, melting temperature and density. Through the application of a consistent methodology, the direct comparison of values in between different PCM is guaranteed. The gathered information will be published in an open-access format to enable researchers and engineers driving the dissemination of latent thermal energy storages further. Thermo-physical properties of alcohols, sugar alcohols, esters, paraffins, fatty acids, eutectics and salt hydrates will be published, where as a systematical selection of PCM per class allows for further analysis.

CONCLUSION: The further dissemination of PCM is only possible if the selected materials exceed not only the characteristics of current applications but also out-perform in terms of reliability and performance. In order to develop those materials a sound selection process is supported through the herein presented library of basic properties. These enable the selection of the most suitable candidates for further development of application-ready materials and thus enabling the dissemination of latent heat storage systems.

A REVIEW ON PHASE CHANGE MATERIALS, UTILIZATION IN THE AERONAUTICAL FIELD.

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Phase Change Materials are gaining a lot of attention these days due to their technology readiness level (TRL) which is close to commercial use for thermal energy storage. In this paper, different types of applications in the aviation field and overall information concerning the promising field of PCMs will be presented. The use of PCMs can enhance many different aspects within the aviation field such as general features, energy storage, and consumption principles. The aviation industry has been a key contributor to global economic prosperity, not only because of the tourism industry boosting local economies but also because it has allowed for improvements to global trade. From economically to environmentally speaking this field plays a pivotal role in our lives. The aeronautical field has risen rapidly over the past two decades reaching nearly 1 Gt of CO₂ emissions in 2019, or about 2.8 % of global CO₂ emissions from fossil fuel combustion, which respectively affects global warming. The high energy density of PCMs and their isothermal performance make them suitable for applications related to the cooling system of electrical engines, turbine inlet chilling with thermal energy storage, and more. There are many different types of PCM materials and the component consistency determines the following material-based division. There are two principal classes of phase change material: organic (carbon-containing) materials derived from petroleum, from plants, or from animals; and salt hydrates, which generally use natural salts either from the sea or from mineral either deposits or are by-products of other processes. The PCM properties are fundamentally affected by the foundation selection. For instance, characteristics such as the melting temperature, heat of fusion magnitude, and thermal conductivity as well, significantly differ. Paraffin wax, non-paraffin organics, hydrated salts, and more are some of the main types of selection mainly affected by the principles and the application of use. The durability of the material through cycles of phase change is a crucial aspect to consider. The durability can also be negatively affected when the PCM undergoes temperatures well above its melting point, as more details will be presented. Therefore, the temperature has to be properly controlled in each corner of the PCM storage to ensure the durability of the system. With all that being said, distinctive attention must be paid to the use of PCMs due to the remarkable working conditions concerning temperature fluctuation during the flight conditions. Creating a self-aware aircraft, able to monitor and report its health status will be a feature enabling force in driving down maintenance costs. Achieving this awareness requires the installation of new innovative systems on specific, crucial, and inaccessible areas of an aircraft. Sensor networking, self-maintaining structural health monitoring, and thermoelectric harvesting systems might be some of them and this is where PCMs come in. Furthermore, studies have shown that structures formed by phase change energy storage materials could transform the aerodynamic heat waste deriving from the aerodynamic heating and temperature shock during complex flight conditions and distinctive thermal gradients into stable electric energy for the internal system. Among the advantages of PCM devices, the stability of temperature control, the absence of moving parts, and a reduced mass are some of them. Phase change materials can be considered as one of the critical components to reach significant results considering the thermal performance of the PCM system in the aeronautical field thus extensive study has to be made.

ENERSTOCK 2021

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ORAL PRESENTATIONS

CARNOT-BATTERIES AND THE DECARBONIZATION OF COAL FIRED POWER PLANTS

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Coal-fired power plants are the largest single emitter of carbon dioxide worldwide. Against this background, Germany is discussing the decommissioning of coal-fired power plants and their replacement by low-carbon sources of electricity. However, such decommissioning incurs high costs and loss of firm power capacity. It is therefore a formidable challenge for energy research to develop cost-effective concepts for decarbonizing these plants. The DLR is currently carrying out research on large-scale electricity storage using the emerging technology of Carnot-Batteries. A Carnot-Battery transforms renewable electricity into high-temperature heat that is stored in low-cost thermal energy storage towers using molten salt at temperatures between 290°C and 565°C or ceramic solid storage with air as heat transfer medium at temperatures up to 750°C. The thermal energy is later transformed back to electricity on demand. Firm capacity can be guaranteed using renewable or fossil resources like biomass or natural gas for backup potentially covering the larger periods of several weeks without reasonable solar and wind resources.

Carnot-Batteries have the potential to solve the large-scale energy storage problem, in order to facilitate the future needs when extending the renewable energy production and use reliable, well known and low-cost components. The necessary storage capacity can be made available through Carnot batteries in short instance using the existing infrastructure of large conventional power plants and the grid connections and the existing experienced staff. Based on its expertise in Carnot-Batteries and thermal energy storage systems for solar thermal power plants the DLR has proposed to convert coal-fired power plants into storage power plants (SPP) by keeping a part of the infrastructure of the old plant and replacing the coal-fired boiler with the thermal energy storage together with leading utilities in Germany and worldwide.

The present communication will provide an overview of the technical features of storage power plants along with estimates of their costs and their role in the decarbonization of the German and global fleet of coal-fired power plants. The communication will also outline a proposal for a “Reallabor” in collaboration with a German utility company expected to provide the first plant-scale demonstration of the DLR concept. Finally, the communication will present the DLR Global Coal Atlas Project that intends to analyze the technical feasibility and the costs of decarbonizing coal-fired power plants worldwide.

DEMONSTRATION OF TWO LATENT HEAT STORAGEES FOR INDUSTRIAL SOLAR PROCESS HEAT APPLICATIONS

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INTRODUCTION: Versatile and economically competitive thermal energy storages are necessary to fulfill the widely differing requirements for thermal storages applied in renewable energy systems. Especially solar thermal installations require thermal storages to be able to achieve high solar fractions.

MATERIAL AND METHODS: In this contribution, we will present work that has been performed within the European project HyCool (<https://hycool-euproject.eu>). Two demonstration sites in Spain have been selected to install an advanced solar heating and cooling system. Fresnel collectors are used to convert solar irradiation into heat. Pressurized water and steam are heated up to 160 °C and 230 °C respectively. One part of the generated heat is directly utilized in the various industrial processes, while the other part is used to drive a hybrid compression-absorption chiller to generate chilled water, which is employed for process cooling.

AIT's role in the project was to develop thermal energy storages for each of the two demo sites to compensate for the intermittent solar radiation. Based on previous projects, we selected the technology of latent heat storages to store heat up to 230 °C.

RESULTS: At the demo site of Bo De Debo, we designed, simulated, constructed, built and installed a latent heat storage based on a fin-tube heat exchanger and high density polyethylene as phase change material based on a design published earlier [1], but with significant technical improvements of various details.

At the second demo site at Givaudan, we adapted another design that we have been developed and published previously [2] based on an inverted shell-and-tube heat exchanger. The storage of Givaudan employs a eutectic LiNO₃/NaNO₃ salt mixture as PCM and is designed to be able to be charged directly with steam. Upon discharging the storage serves as steam generator itself.

We present the system design of both demo sites first and explain the very role of the energy storages and their respective control strategies as well as the details concerning the overall solar heating and cooling system installed at the demo sites.

Then, we explain the technical design of the storages and present a dedicated physical model that was implemented in Dymola/Modelica to actually simulate the complex thermal behaviour of the storage in detail. We present simulation results of different charging and discharging situations including parametric variations and a detailed analysis of the heat transfer within the storage.

Then, we show details of the storage construction and explain the manufacturing process as well as the installation and commissioning process of such latent heat storages directly on site at a real industrial factory. Finally, we present monitoring data and evaluations of storage key performance indicators such as energy capacity, charging/discharging power and heat losses.

CONCLUSION: We conclude by summarizing the results and presenting lessons learnt in order to provide insight for other researchers to further develop this technology and bring forward the field of renewable heat for industrial processes in general.

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DISTRICT COOLING SYSTEM OPTIMIZATION WITH DISTRIBUTED COLD STORAGE ADOPTING POWER-TO-COLD: A CASE STUDY ON NORRENERGI AB

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INTRODUCTION: District Cooling (DC) is gaining momentum today, with growing cooling demands owing to global warming. In Sweden, around 1 TWh of DC [1], [2], caters to service, industrial and commercial sectors [3], [4], while residential space cooling is excluded so far. The total DC demand however is much larger 2-5 TWh [5], with only about 8% annual expansion rate since 2000 [3], thus still not meeting the total potential. Certain Swedish municipalities who do not have DC at all yet are in the process of acquiring such (e.g. e.g. Hässleholm [6]) to address the growing cooling demands. The DC supply mix in Sweden typically is made of free cooling, compression cooling, absorption cooling, and heat pumps [3], [7], [8]. Free cooling is the cheapest mode of cold production with the highest coefficient of performance (COP) today, where the cold from natural water bodies like seas, rivers and lakes is extracted via heat exchangers [3], [8]. Cold storages (CSs) are also an integral part of these DC systems, to lower the capacity installation costs via peak shaving and load shifting. These CSs can be charged using cheaper off-peak electricity (e.g. at night) and/or surplus renewable electricity (using free cooling, chillers and heat pumps), and discharged to cover cooling peaks (e.g. during the day) adopting the power-to-cold concept [9]. The CSs in the Swedish DC systems are almost exclusively centralized larger storages, while interest is emerging today on smaller distributed CSs to recover more local cold surpluses and to optimize the supply better. In this context, this work aims to optimize DC systems with distributed CSs, using the case study DC system of Norrenergi AB, Sweden. Norrenergi AB supplies cold to Solna and Sundbyberg, via three main production plants at Solna, Sundbyberg and Frösunda, employing free cooling, compression chillers and heat pumps, plus one 10 MW (6500 m³) CS in Solna. Their DC production today is already from 100% renewable electricity.

METHODOLOGY: This DC system optimization with distributed CSs was performed using BoFit optimization software, from ProCom GmbH. The base case (BC) was defined considering Norrenergi AB's current DC system (with 10 MW CS in Solna). Four future scenarios (Sc.s) were also defined to account additional CSs integration into this BC, to optimize the cold supply. In these future scenarios, the considered additional CSs are, respectively: one 15 MW at Sundbyberg (Sc. 1), one 15 MW at Frösunda (Sc. 2), and two 3 MW CS at Sundbyberg and Frösunda (in both Sc.3 and Sc.4). These new CSs supply cold to all customers, except for Sc.3 where the new CS supplies only to certain high-demand customers. All these CSs operate adopting power-to-cold concept. The optimization criteria was the cost of electricity to produce the required cold. Here, the electricity prices from Nordpool for SE3 region were used, for a single days' operation using hourly demand data from Norrenergi AB. One of the highest demand day in the recent years, i.e., 02nd of August 2018 (being one of the hottest months in an exceptional warm year) with a 59 MW cooling peak, was chosen as a representative case for this optimization. This was chosen because, if the DC system can cater to the highest demand, it can sustain well for the rest of the demands. In BoFit, for modelling simplification, a number of cooling customers in Norrenergi AB's DC system were aggregated (considering their physical locations) to several 'regions', while each production plant was defined in a 'container' inside which all the cold production units were defined for real-time specifications.

RESULTS DISCUSSION: An energy balance on the modelled data as compared to the real data from August 02 2018 verified the model's validity. The BoFit optimization of Norrenergi AB's DC system with additional distributed CSs, to complement their existing CS of 10 MW (in BC), yielded that all the four scenarios allow cost savings (in-terms of electricity for cold production) of 23%, 4%, 13% and 14% respectively for Sc. 1-4 as compared to the BC with the 10 MW CS in Solna. Thus, the 15 MW CS integration to Sundbyberg yields the best cost-saving.

CONCLUSIONS: The results of this work suggests that installing a 15 MW additional CS at Sundbyberg is the best possible alternative, out of the evaluated scenarios. Analysis of the DC grid dynamics with these additional cold storages is ongoing, to evaluate if the DC grid can accommodate these new CSs' operation, to choose the optimal storage size and location. Their related cost analyses will also be conducted, to strengthen the eventual cold storage choices.

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KEYWORDS: District cooling, cold storage, distributed cold storage, numerical simulation, base case, scenarios

FLEXIBILITY OF REFRIGERATION SYSTEMS FOR GRID BALANCING IN GERMANY

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The increased share of renewable energies connected to the power grid is a significant challenge. Unlike conventional power generation, photovoltaics and wind energy in particular are subject to strong fluctuations and not available appropriate to the demand. Ensuring the security of electricity supply, such grid fluctuations must be compensated. This can be achieved by adapting existing supply systems and developing new ones by making them more flexible and thus more grid-compatible. Refrigeration technology accounts for almost 14 % of total electricity consumption in Germany and it is suspected as a potential field for grid balancing. The research project "flexibilization of refrigeration systems for grid balancing" at the Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT deals with the question how flexible refrigeration systems for grid balancing in Germany are.

At first, a meta-study serves to gain an overview of refrigeration applications in Germany, which applications require refrigeration and what is the cooling demand as well as the final power demand for the cooling supply.

In order to determine the flexibility and the grid-compatibility of such applications, cold load profiles of the applications are required, which characterize the respective cooling applications. The cold load profiles serve as a basis for system optimization and thus for the determination of the grid-compatibility. Furthermore, the load profiles can be used to categorize cooling applications. Applications with similar load curves are gathered to categories or types of application. The categories permit to simplify the application variety and provide a better overview of the refrigeration applications in Germany.

Due to the fact that cold load profiles are not available for all applications, there is a necessity of synthetic cooling load profiles generation. Such a load profile generator is being developed within the scope of the research project and its generation methods presented in this paper. The cold load profile is split into components and the major influencing factors are determined. A mathematical model calculated the load profile for the desired application. For validation, measurements of different applications at different locations are used.

CHEMISORPTION AT SOLID-LIQUID INTERFACES AS A MECHANISM FOR ENHANCED SENSIBLE ENERGY STORAGE IN NANOFLUIDS

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INTRODUCTION: The specific heat of a heat transfer fluid can be occasionally improved by the dispersion of nanoparticles to form a nanofluid, thus enhancing its potential for sensible energy storage without the implication of a secondary medium. This effect has technical and economic significance for thermal management and energy conversion applications, but the associated physical and chemical features explaining it are unclear, thus blocking an optimum exploitation and delaying the transition from basic research to actual application. Here we report results from an investigation on the specific heat of Pd nanoplate-containing aromatic oil-based nanofluids, to be used as heat transfer fluid in parabolic trough concentrating solar power. Experimentally, the specific heat of the samples prepared was found to linearly increase with temperature and to be maximally enhanced at intermediate nanomaterial concentrations. Theoretically, the formation of a layer of chemisorbed base fluid molecules at the solid-liquid interface is proven to be thermodynamically favoured via DFT simulations, and that layer is also proven to be partially responsible of the specific heat enhancement in nanofluids via MD simulations. Our work combines experimental techniques and both ab-initio and classical molecular simulation techniques to prove chemisorption at solid-liquid interface is one of the root causes for enhanced sensible energy storage in nanofluids.

METHODS: Pd nanoplates were synthesised by mild chemical reduction of Pd²⁺ with polyvinyl pyrrolidone in a kinetically controlled hydrothermal process, then isolated in dry powder form and dispersed into a solution 1.0 wt.% of Triton X-100 surfactant in the base fluid DowthermTM A by ultrasonication. The colloid resulting from ultrasonication and its 1:2 and 1:5 dilutions, with mass fractions of 0.060 wt.%, 0.030 wt.% and 0.012 wt.% in Pd nanoplates, are the nanofluids whose specific heat is to be characterised by temperature-modulated differential scanning calorimetry. An in-depth description on the formulation and characterisation procedures is available in literature [1]. The free energies, minimum energy paths, geometries and interaction energy surfaces of the adsorption complexes of diphenyl oxide and biphenyl on both Pd (111) and (100) surfaces were examined by periodic-DFT simulations with VASP [2-4]. The exchange-correlation term was calculated within the generalized gradient approximation using the dispersion-corrected PBE [5, 6] functional. Interactions between valence electrons and atomic cores were described using PAW potentials [7]. The impact of the interfacial molecular layering and other associated variables on the specific heat of nanofluids was assessed on the basis of an energy variance analysis derived from classical MD simulations with LAMMPS [8]. The OPLS-AA force field [9] was considered for bonding and non-bonding interactions between atoms in the base fluid and Morse potentials were also introduced to account for bonding interactions between Pd atoms in the nanostructure and between surface Pd atoms and C atoms of chemisorbed base fluid molecules. An in-depth description on the details and parameters required in DFT and MD simulations is available in literature [1, 10].

RESULTS: The specific heat of nanofluids samples was found to increase by 5.9%, 7.3% and 4.8% at 100.0 °C and 13.9%, 17.4% and 10.0% at 200.0 °C, for 0.060 wt.%, 0.030 wt.% and 0.012 wt.% samples, respectively. Trends with temperature were monotonously linear with the slopes diverging with respect to the base fluid; i.e. the presence of Pd nanoplates increases sensible heat storage for increasing temperatures. Trends with mass fraction exhibited a distinctive maximum for intermediate concentrations, as explained by Hentschke's

model [11]. The adequacy of this phenomenological description allowed us to consider this nanofluid to be a representative case for the study of the interfacial molecular layering. We determined with DFT simulations that diphenyl oxide and biphenyl molecules (in the base fluid) chemisorb on Pd (111) and (100) with no dissociation. The process, with adsorption energies ranging from -3.6 eV to -4.1 eV, is thermodynamically favoured in both cases, with an activation barrier of +0.3 eV for diphenyl oxide due to significant conformational changes in the molecule. This means the chemisorption of biphenyl is favoured over diphenyl oxide and that molecules will not leave the solid-liquid interface once adsorbed, given the energetics of thermal effects are in the order of 41 meV at 473 K. These results allowed us to do advanced modelling of nanofluid systems for MD simulations, from which we rationalised that the specific heat of nanofluids is enhanced with respect to the base fluid due to sensible energy storage arising from the surface of the nanoplate (4%) and also from the interfacial molecular layer and the surrounding molecular mesolayer (by an additional 3%).

CONCLUSIONS: Specific heat of metal-containing aromatic oil-based is enhanced with respect to the base fluid. Here we report a maximum enhancement of 17.4% in this thermophysical property for a Pd content of 0.030 wt.% at 200 °C. We demonstrate that a thermodynamic driving force exists for the formation of a shelter-like layer of base fluid molecules chemisorbed in the solid-liquid interface and that half of the specific heat enhancement is associated to the existence of this interfacial structure around Pd nanoplates. This insight widens the vision of nanofluid researchers by helping on the choice of nanomaterials and base fluids for the performance of nanofluids to be optimised.

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NANOFLUIDS STUDY THROUGH INFRARED THERMOGRAPHY AND PHYSICO-CHEMICAL CHARACTERIZATION

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INTRODUCTION: In the last years, nanofluids has become a promising option for a wide variety of systems [1]. Particularly, nanofluids with improved thermal properties, such as an abnormal increase in heat capacity (Cp)[2,3], become more attractive for the implementation in a great variety of applications that uses heat transfer fluids or thermal energy storage materials. Nanofluids are able to store unexpected amount of energy when around 1 wt. % nanoparticles are added[4]. However, the theoretical explanation of this behavior lacks of a consensus [5]–[7]. We have used infrared thermography supplemented with a physico-chemical characterization to demonstrate the formation of solid-liquid interfaces that directly affects the value of Cp. This study provides an explanation about the abnormal nanofluids behavior.

MATERIALS AND SYNTHESIS: For this study, nanofluids were formulated with 1 wt. % of nanoparticles concentration. Commercial silicon oxide nanoparticles of 5-15 nm of diameter (Sigma-Aldrich, 99.5%) and sodium nitrate (Sigma Aldrich, 99.995%) were used. To synthesize the materials the standard 1-step method was performed[8].

Measurement system

The measurement system consists in infrared thermography, open furnace, control and measurement system and ventilation and safety structure.

Characterization

The nanofluids was characterized by a high resolution (≥ 25 mK) infrared camera (Infratec GmbH). The thermophysical and chemical properties were characterized by differential scanning calorimetry (DSC 822e Star3+, from Mettler Toledo) and FT-IR spectroscopy with attenuated total reflectance, FT-IR ATR (Spectrum TwoTM, PerkinElmer).

RESULTS: The infrared thermography study helps us to deep analyze the melting and thermal behavior of the nanofluids. The SiO₂ nanofluid and the fluid base (NaNO₃) were simultaneously subjected to the same thermal power. The obtained thermography's during the melting process from 150 °C to 320 °C, shows an anomalous behavior in the melting and a regions with decrease in the thermal radiation from the surface as the thermal flow increases (after the melting temperature of the pure NaNO₃). This behavior was attributed to the formation of a semi-solid surface, like a foam. Therefore, the formation of liquid-solid interfaces (LSIs). This layer (new phase) is observed to form from the start of the melting process and to continue up to approximately 400 °C, and at this point the layer melts. The surface layer and the liquid base nanofluid were characterized. By FT-IR were identified characteristics vibration bands, due to the formation of interfacial high specific-surface-area (SSA) silica layer modes in the surface layer. On the other hand, in the calorimetric study an exothermic peak was observed at 350 °C, identifying the liquid-solid transition due to the layer formation. Finally, the Cp enhancement was calculated for the surface layer of 2.2 J/g·K in front of the 1.1 J/g·K of the liquid base. Consequently, an enhancement of 100% of the formed layer was identified, generating a fluid with a high thermal interface.

CONCLUSIONS: This study demonstrates experimentally the formation of a surface layer. This layer involves the formation of liquid-solid interphases (LSIs) with high-energy vibration modes and the presence of thermal boundaries (kapitza resistance). The LSIs, increases the number of degrees of freedom and directly influence in the heat capacity of the system, justifying the abnormal behavior of nanofluids. Furthermore,

some theoretical studies suggested the formation of a layer around the nanoparticles, but none had demonstrated it experimentally.

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COMMISSIONING OF HIGH TEMPERATURE THERMAL ENERGY STORAGE FOR HIGH POWER LEVELS

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INTRODUCTION: A high power and capacity PCM storage unit has been integrated into a heat- and power cogeneration plant in Saarland, Germany. This storage will act as an intermediate back-up to a heat recovery steam generator and gas turbine and is therefore situated in parallel to this unit, also between the feedwater pumps and the steam main. The steam required is superheated at 300°C and 26 bar, resulting in a maximum thermal power of 6 MW. The storage needs to provide a minimum capacity of 1.5 MWh. Operation of this storage unit will increase efficiency and decrease fossil fuel use by reducing the use of a conventional back-up boiler. The filling of the unit with ~32 t of storage material in conjunction with the commissioning of the storage unit is in process and initial data has been acquired. These data will be analyzed and presented. This is part of the project TESIN, funded by the German Ministry of Economic Affairs and Energy.

METHODS: During the filling and commissioning phase, the PCM storage unit is filled with sodium nitrate salt particles and heated until these particles melt, iteratively until the storage unit is full. During the charging and discharging processes conducted for the filling process, initial insight into the valve dynamics can be gained, as well as limit adjustments made for the control plans, as the main process of discharging and charging will later be automatic. Data is continually acquired throughout this process, so that initial information regarding the storage unit characteristics can be analyzed.

RESULTS: An extended finned tube storage unit was built and integrated into an operating power plant. During the first heating of the storage unit at approximately 55% fill level of PCM, steam was produced for the first time, and the initial data show a temperature front moving vertically through the storage unit during heating of the unit.

CONCLUSIONS: The integration and initial commissioning of the storage unit has been successfully concluded, so that the storage unit filling and control optimization can be finalized. Thereafter, a test spectrum will be conducted in order to characterize the storage unit, followed by standard operation in the power plant. In this presentation, data and experience from the commissioning process will be shown and discussed.

ENHANCING ENERGY DENSITY OF EXISTING SENSIBLE THERMAL STORAGE SYSTEM WITH ENCAPSULATED PCM

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INTRODUCTION: In past decades many types of research have been done on PCMs for thermal storage in building's systems for use in new or existing building applications [1]. According to the European Technology Platform on Renewable Heating and Cooling further research on mechanisms of integrating PCMs into existing heating and cooling systems is one of the priorities for research on latent thermal storage. Furthermore, the emphasis is given to encapsulation and stabilisation of PCMs, in particular of salt-hydrates, which are cheaper than paraffin and does not present the fire risk [2]. He et al. experimentally investigated the performance of a water thermal storage tank with a packed bed of encapsulated paraffin wax. The 0.75 m³ water storage tank was filled with encapsulated PCMs with phase change temperature at around 68°C. During the 37°C/70°C discharging process the duration of outlet temperature from the thermal storage tank above 67°C is extended by 18% at the low flow rates in comparison to water thermal storage tank [3]. Zhou et al. investigated a centralized solar hot water system for residential buildings with spherically encapsulated paraffin wax with a phase change temperature of 60°C. The average solar fraction of a system without PCM was 51% while it increases to 80% when using PCM [4]. Compared to water heat storage tank, researches on encapsulated PCMs inside water heat storage tank are limited and most of them are numerical simulations instead of the experimental study [3]. The researches on water thermal storage tank with encapsulated PCMs are also manly done for a heating system with an operational temperature above 40°C or for bellow 0°C. Therefore, the need for experimental research of a centralized latent thermal storage system for low-temperature heating or high-temperature cooling system for residential buildings is needed in a way to provide practical improvement of the energy density of existing water thermal storage system. The latter is especially needed in retrofits of residential buildings due to the RES system integration, where higher volumes of water thermal storage are needed in order to level out the mismatch between supply and demand [5]. Therefore the objective of the present research is to enhance the energy density of the existing water thermal storage system by integrating encapsulated PCM (salt-hydrate mixture) and experimentally investigate its performance for usage in low-temperature heating systems.

MATERIALS AND METHODS: The system consisted of three 100 litres tanks connected in series where encapsulated PCMs were inserted inside each tank. PCM was encapsulated in spherical modules made of high-density polyethylene (HDPE) with a diameter of 80 mm. Inside each tank, 192 spheres were inserted what represented 31 litres of PCM in one tank and 576 spheres and 93 l of PCM in the whole system. This represents 37 % of PCM according to the total thermal storage volume. PCM that was used in the research was a salt-hydrate mixture with phase change temperature around 25°C with melting enthalpy of 271 kJ/l and specific enthalpy of 300 kJ/l in the range of 15 K. At first measurements with only water as a thermal storage medium were carried out and afterwards measurements with the inclusion of PCM capsules inside the water tanks were carried out. Water temperatures were measured at the bottom, middle and top of each tank and at the inlet and outlet of the thermal storage system. The water flow rate was measured at the inlet of the system and was set to be constant during the experiment. In both cases, operational conditions were the same. The thermal storage system was heated on 35°C and discharged with an inlet water temperature of 15°C to the final temperature of 17°C. Discharged heat from both systems was calculated and compared.

RESULTS: At discharging process of heat from 35°C to 17°C, the discharged heat from the thermal storage system was 7.6 kWh and 12.8 kWh for the water thermal storage system and latent thermal storage system respectively. This result shows that at the same operating conditions with the temperature difference between initial and end thermal storage temperatures of approximately 18 K, the latent thermal storage provides higher discharged heat for 68% in comparison to the water-only thermal storage system.

CONCLUSIONS: The results from the present research showed that the inclusion of 37 % of PCM that is encapsulated in spherical modules led to 68 % higher thermal storage in comparison to the water-only system. This results showed that at the same operating conditions, thermal storage volume can be reduced by up to 68 % if PCMs are inserted inside the water thermal storage system. This provides increased energy density that is needed when integrating RES systems in retrofits of the buildings where space constrains represents a common issue. This means that there is not enough space to install a water thermal storage system, but there is a need to store a sufficient amount of heat or cold to level out the mismatch between the supply of RES and thermal demand of the building. This kind of latent thermal storage solution with spherically encapsulated PCM can be used for low-temperature applications with a smaller temperature difference in water heating and cooling systems. Besides the function of heat transfer fluid, the water also has a function of thermal storage medium what provides higher thermal power needed at the beginning of the discharge compared to some commercial solution of a compact latent thermal storage solution, where PCM represents around 90% of total volume. Furthermore, commercial solutions with integrated encapsulated PCMs operate at a higher temperature level and a bigger temperature difference.

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EFFECT OF FLUID VELOCITY ON STORAGE PERFORMANCE OF MEDIUM TEMPERATURE PACKED-BED THERMAL ENERGY STORAGE SYSTEMS

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INTRODUCTION: Variability of sunlight is the main barrier for continuous exploitation in industrial processes. Thermal energy storage (TES) is the key technology to provide continuous energy from solar systems. Packed-bed is a promising TES method for medium-high temperature applications by using low cost storage material as packing. The performance of a packed-bed TES system depends on several factors such as heat transfer fluid (HTF) flow, inlet temperature, thermophysical properties of storage materials and HTF, porosity, dimensions of storage material and tank (Marti et al., 2018). There can be many feasible operating parameters for a TES system and some are better than the others. Numerical modeling and cycling experiments can be carried out to determine the optimum parameters. Lugolole et al (2019) found that rate of thermal energy and exergy of oil/rock packed-bed system is higher at the lowest flow rate. Oro et al. (2013) reported that higher stratification numbers were found at lower flow rates of packed-bed TES system. Bruch et al. (2017) observed that performance of oil/rock TES system decreases at the lowest and highest fluid flow rates. In this study, performance of lab-scale packed-bed TES system using a new demolition waste based material was investigated experimentally for different HTF flow rates.

MATERIALS AND METHODS: Laboratory scale packed-bed TES system with a cylindrical tank of 0.3 m diameter and 0.9 m height was built to analyze its performance in industrial processes below 200 °C. Novel storage materials with a heat capacity of 4140 kJm⁻³K⁻¹ developed from demolition wastes were filled in the storage tank with a bed void fraction of 0.39. Therminol 66 synthetic oil was used as HTF.

The performance on lab-scale packed-bed TES system was investigated experimentally at an inlet temperature of 160°C for HTF flow rate up to 750 kg/h. Maximum energy (E_{max}) that can be stored in packed-bed system is the sum of energy stored in solid phase, fluid phase and other components such as tank walls, filters.

The energy stored during charging (EC) and discharging steps (ED) is the sum of stored energy in fluid phase to the time at the beginning and at the end of a given charge or discharge (Bruch et al. 2017).

The ratio of ED to, EC is defined as the energetic efficiency by Bruch et al. (2017). The system energy efficiency can be written as the ratio of ED to E_{max} (IEA-ECES, 2018). The stratification number, is the ratio of the mean of the temperature gradients at any time t to the maximum mean temperature for the charging and discharging steps (Fernandez Seara et al. 2007).

RESULTS: Measured temperature profiles at the center of the tank at different HTF flow rates were investigated. Smooth stratification behavior with no deviations was observed at 50 kgh⁻¹ flow rate for charging and discharging processes. But, during charging process, when flow rate was increased to 750 kgh⁻¹, stratification started to deteriorate due to the mixing fluid at unsteady laminar flow.

In thermocline packed beds, good thermal stratification increases the performance of the TES system (Hollands and Lightstone, 1989). The stratification number as a function of dimensionless time for HTF flow rates up to 750 kg/h during charging and discharging experiments were determined. It was found that stratification numbers decreased when flow rate increased due to the better mixing fluid at higher flow rates. Same conclusion was achieved by Oro et al. (2013), Fernandez-Seara et al. (2007); Lugolole et al. (2019).

The cumulative energy stored during charging and discharging were calculated. It was clearly seen that the EC and ED varied with fluid flow rate. EC can reach to 7.27 kWh at flow rate of 500 kg/h and ED can reach to

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6.17 kWh at flow rate of 750 kg/h. As flow rate was increased from 50 kg/h to 750 kg/h, the charging and discharging durations decreased dramatically from 120 min to 20 min. The increase in flow rate decreased heat losses with shortening of cycling time and increased energy stored.

Although, the charging step is completed in a shorter time with lower heat loss, pressure drop can increase with HTF flow rate. Besides, higher flow rate causes disruption of laminar flow due to the increase in particle Reynolds number. Maximum storage performance ($\eta_{\text{sys}}:67.0$, $\eta_E:96.8$) was observed at $\dot{m}:250$ kg/h when flow regime was still laminar ($Re_p < 10$) and heat loss was lower as also observed by Erregueragui et al. 2016; Bruch et al., 2017.

CONCLUSIONS: Performance of the lab-scale packed bed TES system filled with novel STESMs prepared from demolition wastes with diameter of 0.01 m was investigated experimentally. Experimental results were analyzed based on fluid flow rate in a range of 50 kg/h to 750 kg/h at a constant fluid temperature of 160 °C. Although, the best stratification behavior was observed in lower HTF flow rate, high heat loss due to long cycle time reduced the storage capacity. Energy efficiency of the system reached to maximum level (67%) at charging temperature of 160 °C and flow rate of 250 kg/h.

THERMAL HIGH PERFORMANCE STORAGEES FOR ELECTRIC BUS HEATING - OVERVIEW ON THE CURRENT STATE OF DEVELOPMENT

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INTRODUCTION: Battery electric buses are facing huge challenges when interior heating is required on winter term conditions, since the heating demand can exceed the power that is required for traction. As state-of-the-art solutions for providing interior heating, diesel fueled heaters, electric resistance heaters or electric heat pumps are used. However, when using diesel fueled heaters, local emissions are emitted. When using electric resistance heaters, electric energy from the battery is consumed cutting the range of the vehicle up to more than 50 %. When using heat pumps, overall energy consumption for interior heating is reduced as well as range reduction. However, it is still very significant on cold ambient conditions. Additionally, a second heater has to be used, since the thermal output of available heat pumps is not sufficient on temperatures below -10 °C.

To overcome this challenge, the use of a Thermal High Performance Storage (THS) as stand-alone heating solution or additional heater can be used, as already proposed in past publications. The THS can be electrically charged simultaneously to the traction battery. The stored energy afterwards is used for heating the interior. The benefit of using a THS for interior heating is that no local emissions occur and no energy from the battery has to be used for heating. Compared to currently used batteries, a THS can be up to 90 % cheaper, 50 % lighter and 40 % smaller.

Materials and Methods: Within the targeted oral presentation, an overview on the state of development of THS for the application as bus heating system will be given. For this, the THS will be split in its single components storage material, housing, charging system and discharging system. Also, a look on design considerations for the overall assembly is given.

RESULTS: Regarding storage materials, the most suitable metallic Phase Change Materials (mPCM) will be shown and the current state of investigation of their thermophysical properties. Regarding housing, the problematic of potential reaction with the mPCM is addressed. Potential solutions of how a suitable housing container has to be designed will be shown. For charging, electric resistance heating or inductive heating are potential solutions. The potential of solutions regarding power density is shown as well as advantages and disadvantages of both solutions for the described application. For discharging, several concepts using liquid fluid, gaseous fluid or the phase change of a working fluid are considered. For this, different solutions and their potentials will be shown as well. Last thing to be presented are considerations concerning the overall assembly of the storage system. Especially the relative position of the discharging system to the charging system is of main interest, due to the formation of materials defects and its high impact on the power density.

CONCLUSION: Thermal High Performance Storagees could be a highly relevant solution to solve the issues regarding interior heating of battery electric buses. The current state of development underlines the potential of this technology, however also shows the challenges on the further development.

AN INSIGHT INTO CHALLENGES ASSOCIATE WITH SEASONAL STORAGE IN SOLAR DISTRICT HEATING SYSTEMS

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A promising pathway towards sustainable transition to clean energy production lies in the adoption of solar assisted district heating systems (SDHS), which are placed in the end-user sector and hence reduce energy transmission losses. However, SDHS technical barriers during their design and operation phases, combined with their economic limitation, promote a high variation in quantifying SDHS benefits over their lifetime. This study proposes a complete framework using a robust machine learning approach based on an artificial neural network (ANN) to inherent sustainability principles in the design of SDHS. These principles comprising the life cycle cost analysis and the life cycle assessment are formulated in a multi-objective optimization problem to assess the SDHS beneficial performance in comparison to conventional heating systems based on natural gas. Moreover, the methodological framework investigates the uncertainty in the context of SDHS design, in which the Global Sensitivity Analysis (GSA) based on Bayesian analysis of computer code outputs is combined with the Heuristics optimization frameworks using the low computational expenses benefits of the ANN model.

The application of the framework is illustrated through a case study for the optimal design of SHDS at different urban community sizes (10, 25, 50, and 100 buildings) located in Madrid. The optimization problem is formulated under two optimizations setting where the first setting includes only the system equipment sizing, whereas the other setting embraces the seasonal storage tank (SST) construction materials as well in the optimization problem. Results reveal a substantial improvement in environmental benefits for deploying SDHS instead of the natural gas boilers with the increment in the community size, especially with including the SST construction properties in the optimization problem, and it can achieve an improvement up to 89.3% in the community size of 100 buildings. Moreover, SDHS can reduce the greenhouse gas payback period up to 3 years for all community sizes. These benefits are extended to the economic objective and are reduced up to 30.7-66% based on the community size. In terms of the economic payback period, SDHS show their feasibility when increasing the community size; the payback period can reach 13.7 years at the community size of 100 buildings. Regarding the technical performance, optimization results show that the solar fraction did not fall below 82.1 % for the investigated community sizes with efficiency for the SST above 69.5%. Finally, GSA results indicate the initial investment cost of the SST and its relevant construction materials, in addition to the annual natural gas inflation rate, are primarily responsible for the variability in the optimal system feasibility. The proposed framework based on the robust machine learning approach can provide a good starting point to solve the enormous computational expenses drawbacks associated with the heuristics optimization approach. Furthermore, it can function as a decision support tool that retrofits efforts toward the most effective action plans to fulfil the European Union energy targets regarding clean energy production.

HYBRIDISATION OF LATENT AND THERMOCHEMICAL THERMAL ENERGY STORAGE: 3 IN 1 THERMAL ENERGY STORAGE

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INTRODUCTION: Given that ~90% global energy budget centres around thermal energy generation, transmission and storage, Thermal energy storage (TES) will have a great role to play in future energy systems. TES can be classified into three categories: sensible, latent and thermochemical storage. Sensible heat storage has been in large scale industrial applications for over 200 years (e.g. blast furnace ironmaking); latent heat-based TES has just started to be used in industry, whereas thermochemical based is currently at a low technology readiness level (TRL). Significant research efforts are needed to address some fundamental challenges such as heat and mass transfer limitations [1], [2], difficulties in the temperature control during the charge/discharge processes, life span and cost-effectiveness. The work reported in this paper concerns the combination of latent heat and thermochemical based TES in one stand-alone system. This combination has the potential to address these challenges. Our work aims to integrate thermochemical and latent heat storage materials with an eventual goal to maximise the system-level energy density while maintaining the controllability of the charging/discharging process and enhancing the efficiency at system level. The system allows 3 different configurations where the charging and discharging temperatures are given by the different PCM's melting point and TCM's reactions temperatures.

We report here some preliminary work on a cascading configuration. Such a configuration allows a broad range of TCM/PCM materials selection with no requirements for temperature match. The melting point of the PCM lies in between the discharging-charging process of the TCM, the system is charged and discharged at two different temperatures allowing to have two input/output temperatures. Thereof, the cascade system will be able to store a large amount of energy in a wide temperature range. The PCM will firstly store heat at the melting point, increasing its volume during the phase transition. Then, after the TCM's charging temperature, both PCM and TCM keep this energy within the system. When desired, the temperature of the system will decrease discharging, in the first place the PCM, and eventually, the TCM at its discharging temperature.

MATERIALS AND METHODS: The TCM selected for the proof of concept was magnesium sulphate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), analytical reagent grade (CAS: 10034-99-8, MW: 246.48) supplied by Fisher ScientificTM. The high-density polyethylene (HDPE; CAS: 9002-88-4, MFI: 3.2) was used as the PCM and supplied by Matrix company©.

Different ratios of magnesium sulphate heptahydrate (80–95 wt.%) and HDPE, both in powder form, were mixed. $0.8 \text{ g} \pm 0.05 \text{ g}$ was then pressed into a tablet shape with 13 mm diameter and ~10 mm height using a Lloyd LS100 Plus Materials Testing Machine supplied by Lloyd Instruments company (UK). The operating pressure and holding time was set to 90 MPa and 1.2 min, respectively. Three pellets for each of the formulations and cycling testing were prepared. The compacted composites were tested to determine the cycling stability after 1, 5, 10 and 15 charging/discharging cycles. The latent heat, the enthalpy of reaction and the sensible heat of the TCM/PCM formulations were measured over 30-250°C by using a Netzsch STA 449 F3 Jupiter.

RESULTS: The working pairs that withstand the highest number of cycles were the 80/20 and 85/15. The criteria to select the best working pairs was to consider just the ones that did not show any cracks or major structural problems such as leakage or breakage. In the first selection stage, the structural integrity was

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Oral lectures

prioritised over other attributes, and only the pellets that maintained their structural integrity up to 15 cycles were fully characterised. The energy stored by the pure composite (tested in powder form) after the first dehydration cycle is 18% higher than the composites (cycled in tablet form in the humidity chamber).

CONCLUSIONS: This work validates with a proof concept concept the hybridisation of TCM and PCM materials for TES using HDPE as PCM and magnesium sulphate heptahydrate as TCM. Our preliminary results show that the composite with 20% of PCM presents the highest energy density and maintains structural integrity after 15 cycles, suggesting the feasibility of the hybrid system.

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SYNTHESIS AND CHARACTERIZATION OF MICROCAPSULES BASED ON INORGANIC@PCM FOR THERMAL ENERGY STORAGE AT LOW TEMPERATURE APPLICATIONS

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INTRODUCTION: Due to the exponential increase in the pollution during the last decades, greenhouse gases emission has increased in an incommensurate way. To lessen the negative effects of fossil fuel use, technologies for the use of renewable energy sources have been improved. However, due to the intermittency of these sources, new materials for energy storage have been developed. One of these is the use of phase change materials (PCMs) for thermal energy storage. These materials are capable of absorbing and releasing latent heat through phase transitions [1]. In general, the most used PCMs are those with a phase change from solid to liquid, as they have an energetic process very useful for being used as thermal energy storage. The most used materials are hydrocarbons, as they have high energy density and melting points to cover a range of temperatures between 273 and 333 K, typical in keeping heat in household constructions. [2] But this kind of materials cannot be used in construction if they are not confined. So, recent studies are focused on the design and manufacture of microcapsules, which contain PCMs, based on different inorganic materials such as metal or metal oxides for the storage of thermal energy.

MATERIALS AND METHODS: Paraffina with different melting points to cover a range between 273 to 333 K were used as PCM to be incorporated in the core of microcapsules. To prepare the metal/metal oxide covering of the microcapsules, inorganic salts of Cu and Ni were used as precursors. Synthesis of PCM@metal/metal oxide has been prepared through the in-situ precipitation and hydrothermal reaction using the emulsion templating self-assembly methods. To prepare a proper PCM emulsions in water, optimized magnetic stirring and ultrasonic bath were used. Also, to form the emulsion and the template for the shell structure, different ionic surfactants were used as emulsifiers.

Scanning Electron Microscopy (SEM) along Energy-Dispersive X-ray (EDX) was conducted to analyse the morphology and surface elemental distribution of microcapsules. The crystalline structure of synthesized material was performed by means of X-Ray Diffraction (XRD), and Fourier-transform Infrared Spectroscopy (FTIR) was analysed to characterize the chemical structures of microcapsules.

The phase change behaviour, grade of encapsulation, and thermal stability of microcapsules were studied using Differential Scanning Calorimeter (DSC). In order to determine the heat capacity, Temperature Modulated Differential Scanning Calorimeter (TM-DSC) was used.

RESULTS: The SEM images of the samples showed microcapsules with an irregular polyhedral morphology and sizes between 2 and 3 μm . The formation of microcapsules could be supported observing the presence of some broken microcapsules. Elemental composition measured by means of EDX showed the presence of metals and oxygen in the surface of the microcapsules. FTIR spectroscopy was measured to characterize the chemical composition of synthesized microcapsules. A series of absorption bands were found for all the samples between 3000 and 2850 cm^{-1} , at 1600 cm^{-1} , 1500 and 1400 cm^{-1} and 720 cm^{-1} , characteristic of the paraffin hydrocarbons. Furthermore, a broad band below 700 cm^{-1} typical of metal oxide is identified in all cases. The formation of crystalline metal/metal oxide structures were analysed and confirmed by means of XRD patterns. The presence of paraffin was identified for microcapsules prepared with the paraffin with the highest melting point.

The temperatures and the enthalpy of the melting and freezing process were measured using DSC for the synthesized microcapsules and the different paraffins. Moreover, changes on the phase change

ENERSTOCK 2021

Oral lectures

temperature, the efficiency of the encapsulation (E_{en}) and the energy density of the prepared material were analysed. The results showed a E_{en} around 46% and an energy density of 96.7 J/g. Thermal stability of the materials was evaluated through 30 cycles of heating/cooling and compared with the pure paraffins. Also, isobaric specific heat of the microcapsules was measured, and an improvement compared with the metal/metal oxide due to the PCM in the core of the microcapsule was found.

CONCLUSIONS: Metal/metal oxide microcapsules were successfully synthesized by means of a simple method using the emulsion self-assembly technique. The formation of metal/metal oxide shell and the crystalline structure were confirmed using EDXFTIR spectroscopy and XRD. Also, XRD patterns and FTIR spectra revealed the presence of paraffin in the prepared microcapsules. The morphology was identified as an irregular polyhedral using SEM, and confirmed the formation of microcapsules by observing broken microcapsules. Analysis of DSC cycles showed that microcapsules presented a good thermal stability and energy storage. Finally, isobaric specific heat of metal oxide was improved due to the PCMs in the core of the microparticles.

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HIERARCHICAL MACRO-NANOPOROUS METALS FOR SHAPE-STABILIZED PHASE CHANGE MATERIALS WITH HIGH ENERGY CAPACITY, ENHANCED THERMAL CONDUCTIVITY AND SUPERIOR ANTILEAKAGE PERFORMANCE

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INTRODUCTION: Solid-liquid phase change materials (PCMs) are a convenient solution for latent thermal energy storage due to their great variability, cyclability and high energy capacity achieved in a narrow temperature range. However, low thermal conductivity and leakage issues strongly limit the practical implementation of PCMs. Impregnation into a porous matrix is a promising way to stabilize the shape of PCMs (suppress leakage), as well as enhance thermal conductivity. However, this approach suffers from antagonistically coupled energy capacity and antileakage capability. More specifically, macroporous materials permit high impregnation fraction of PCM (hence, high energy capacity), but do not provide sufficient antileakage capability due insufficient capillary forces. On the contrary, nanoporous materials provide superior antileakage performance due to strong capillary forces, but the impregnation fraction is typically small and nanoconfinement largely inhibits the enthalpy of solid-liquid phase transition (low energy capacity). We recently demonstrated that a new type of material – multimodal hierarchical macro-nanoporous metals [1, 2] – can efficiently resolve the compromise between energy capacity and antileakage performance [3]. This presentation provides, our latest findings within this strategy.

MATERIALS AND METHODS: Multimodal hierarchical porous copper was synthesized by dealloying Cu-Mg, Al-Cu-Mg or Cu-Mg-Zn alloys of close-to-eutectic composition and vacuum impregnated with paraffin wax (melting temperature of 53-58 °C) according to the protocols described elsewhere [1-3]. The obtained shape-stabilized PCMs were subjected to thermal cycling (25 – 75 °C) and characterized by SEM, TEM, XRD, DSC, Flash method, nitrogen adsorption, thermogravimetric analysis. Applicability of the obtained composites for a battery pack thermal management was demonstrated by CFD modelling.

RESULTS: the synthesized copper samples demonstrated 90vol% trimodal hierarchical porosity with the largest pores of ~10-200 µm, medium pores of ~1-3 µm and the smallest pores of ~10-30 nm. Volumetric energy capacity of (copper + paraffin) composites was ~90% of the pure paraffin. The composites were stable and showed no leakage after 50 heating-cooling cycles, which was experimentally and theoretically related to the presence of nanopores. Moreover, thermal conductivity was enhanced more than 3 times compared to pure paraffin. Due to the improved heat transfer and high energy capacity the (copper + paraffin) composite maintained the temperature of the battery pack within the safety limits, contrary to the pure paraffin.

CONCLUSION: Hierarchical macro-nanoporous metals are proposed for shape-stabilized PCMs with high-energy density, enhanced thermal conductivity and leakage-free performance. Such composites can be used for latent TES, being particularly suitable for thermal management of electronics or batteries.

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Oral lectures

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EVALUATION OF NITRATE SALTS AS STORAGE MEDIUM FOR ACTIVE LATENT HEAT THERMAL ENERGY STORAGE SYSTEMS

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INTRODUCTION: In active latent heat thermal energy storage (ALH-TES) systems the phase change material (PCM) is transported through a heat transfer section where the phase change takes place. Compared to passive storage systems where the PCM is stationary, ALH-TES offers an improved operational behavior and allows the separation of the storage material from the heat transfer component. DLR is working on concepts for ALH-TES systems, this includes also the identification of suitable PCMs for the medium and high temperature range. Therefore, a theoretical evaluation was carried out according to the requirements of the ALH-TES systems, i.e. the PCM must operate and be thermally stable in atmospheric conditions between 200 °C and 600 °C. LiNO₃ and NaNO₃ were selected as possible candidates and the results of further evaluation of these two PCMs are shown in this study.

MATERIALS AND METHODS: LiNO₃ and NaNO₃ Suprapur® Merck (Germany) were used for this study in order to compare the results with those available in the literature. The melting temperature and enthalpy were measured using TG-DSC techniques (sample size: milligram scale). The thermal stability of both materials was evaluated performing 10 cycles between 200 °C and 600 °C in a furnace under atmospheric conditions (sample size: gram scale). The melting temperatures were measured in the DSC taking 10 milligram samples after every cycle. To quantify the potential size reduction of ALH-TES system compared to passive latent heat and sensible heat TES systems, the volumetric storage capacities (kWh/m³) were calculated for both materials.

RESULTS: The melting temperatures and enthalpies measured in this study are in good agreement with those results previously reported. For LiNO₃ $\vartheta_M=252.6$ °C, $\Delta FH=352$ J/g and, for NaNO₃ $\vartheta_M=305.7$ °C, $\Delta FH=174$ J/g. The volumetric storage capacities are 631 kWh/m³ and 473 kWh/m³ for LiNO₃ and NaNO₃, respectively.

As a result of the cycles between 200 °C and 600 °C a slight change in the melting temperature was observed in the DSC measurements. To reduce the decomposition rates of the salts and potential corrosion of construction systems, the maximum operating temperature of the ALH-TES system should be set to 560°C when using nitrate salts. This will reduce the storage capacity in 6 % and 8 % for LiNO₃ and NaNO₃ respectively. However, considering LiNO₃, this still means that the volumetric storage capacity is 250% larger than that of the solar salt in the temperature range of 265 °C-565 °C used in sensible heat TES systems.

CONCLUSIONS: LiNO₃ and NaNO₃ fulfill all the technical requirements to be used as storage medium for ALH-TES systems. The maximum operating temperature should be limited to 560°C in order to reduce the degradation of materials over the cycles and thus, also prevent possible corrosion of the construction materials.

EFFECT OF ADDING EXPANDED GRAPHITE MICROPARTICLES IN ORGANIC PLASTIC CRYSTALS FOR LATENT HEAT STORAGE

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INTRODUCTION: Neopentylglycol (NPG) and tris(hydroxymethyl)aminomethane (TRIS) are promising phase change materials (PCMs) for thermal energy storage. These latent-heat based materials undergo reversible solid-solid phase transitions characterized by high enthalpy change (119,4 J/g for NPG and 280,7 J/g for TRIS)[1]. However, a desirable property of latent heat storage systems is an isothermal temperature of transition not achieved in these molecules due to the subcooling phenomena, leading to a lower temperature in the discharge transition [2]. The main objective of this study was the mitigation of the subcooling phenomena in both NPG and TRIS plastic crystals by adding different types and different concentration of expanded graphite microparticles. The goal was to create intermolecular anchor points in order to decrease the mobility of the system thus assisting the phase change during cooling.

MATERIALS AND METHODS: Pure NPG and TRIS were analysed with no pre-treatment. Expanded graphite microparticles (D50 = 75-600 µm) were dispersed in the solid NPG and TRIS by manual mixing. Then the mixture was subjected to a slow (1°C/min) heating/cooling cycle up to the melting. The subcooling degree in the final plastic crystal-expanded graphite composite was analysed by differential scanning calorimetry. Information about enthalpies and temperatures of transition were also obtained.

RESULTS: The optimization of the amount and type of expanded graphite allowed to reach an improvement of the subcooling degree up to 40%. This result was achieved in case of NPG/EG75 composite with 10 wt.% of expanded graphite. Nevertheless, for this composite, a substantial subcooling improvement (30%) was obtained with only 1 wt.% of EG75. For all the composites, reproducible phase transition temperatures and enthalpies are observed. It is worth noting that the higher the initial subcooling degree, the higher the subcooling improvement achieved. This is, the improvement in the TRIS subcooling (with higher undercooling degree than NPG) is higher than that of NPG.

CONCLUSIONS: All these new stable and cyclable composites showed an improvement in the subcooling degree of both NPG and TRIS. Due to the high values of enthalpy, these organic composites are promising candidates for thermal energy storage applications.

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USE OF A SIMPLIFIED NUMERICAL MODEL FOR THE THERMAL PERFORMANCE EVALUATION OF A TUBE&SHELL LHTES

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INTRODUCTION: Thermal energy storage (TES) systems play a key role in CO₂ emission reduction strategies and the use of renewable energy sources. Since latent heat thermal energy storage (LHTES) systems use a phase change material (PCM) as a heat storage medium (HSM), they are currently the subject of important international research studies for their intrinsic high storage capacity. The LHTES performance is typically carried out in an experimental way, as well as with numerical analysis. These numerical studies involve two kinds of models: some suitable only in the description of the conductive thermodynamic behaviour and others, more complex, for simulating fluid dynamic trends (CFD). The first do not take into account the heat transport related to possible mass transport of the PCM in the liquid phase, underestimating the performance of the LHTES system. The second, able to simulate the heat exchange due to the convective motions, are more accurate but need many computational resources in terms of power and computing time. The need for huge computational resources can make these CFD simulations very difficult in the case of systems with not simple geometries and not small dimensions.

MATERIALS AND METHODS: In this work, the possibility of using the first type of model is investigated, in which the simulation is purely conductive, taking, however, into account the contribution of the convective heat exchange within the PCM. These models are based on the “effective thermal conductivity method”. In this method a correlation for the Nusselt number is used to insert the natural convection effect into thermal conductivity coefficient; therefore, a modified thermal conductivity is considered for the PCM while this is in its liquid phase, whereas when the PCM is in its solid phase the thermal conductivity of the base material is used. Three models of the same vertical section of an LHTES tube&shell system have been built. The first, a CFD model, is able to simulate the presence of convective motions. The second, only a conductive model, with effective thermal conductivity and finally, the third model, again conductive, adopts a non-modified thermal conductivity for the PCM. The geometry of the models consists of a cylinder, filled with PCM, with a coaxial tube in which the heat transfer fluid flows. A diathermic oil is used as heat transfer fluid and the solar salt, a mixture of sodium nitrate and potassium nitrate (60-40%wt), is used as PCM. Since this study is interested in the behaviour of the PCM, only this material is simulated, while the effect of the heat transfer fluid is taken into account through a boundary condition of convective heat flow alone. These models have been used to simulate both the charge and the discharge phase of the system. The simulations have been performed using the COMSOL Multiphysics Ver 5.2 calculation code.

RESULTS: The comparison of the results obtained from the CFD simulation (convective model) with the non-modified thermal conductivity model shows how the convective motions accelerate both the charge and the discharge of the system, although the latter to a lesser extent. The CFD model is closer to actuality but required more computational resource than the conductive model. The analysis of the result of the modified thermal conduction model shows how the use of the effective thermal conductivity method allows to obtain a better evaluation of the thermal trend than the model using the basic thermal conductivity of the PCM with a similar computational weight. While improving the forecast, this model also overestimates the characteristic times of the LHTES system in comparison with the CFD model that was used as a reference. However, the use of the model with the effective thermal conductivity method allows to obtain a sensitive reduction in errors in the estimate of both charge and discharge time of the LHTES system.

ENERSTOCK 2021

Oral lectures

CONCLUSION: The first sizing of an LHTES system is currently carried out using conductive type models, thus neglecting the presence of convective motions. This involves an overestimation of both charge and discharge times of the system, and consequently a non-optimized sizing of the LHTES system. The use of an effective thermal conductivity model allows a better evaluation of the thermal performance of the storage system, avoiding the CFD models use that require high computational resources.

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LIFE CYCLE ASSESSMENT (LCA) OF CONCENTRATING SOLAR POWER (CSP) PLANT IN TOWER CONFIGURATION WITH AND WITHOUT THERMAL ENERGY STORAGE (TES)

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INTRODUCTION: The main objective of the present study is to compare the 30-year life cycle assessment of two concentrating solar power systems with tower configuration, one without thermal energy storage and the other with thermal energy storage, in order to assess their potential impact on the environment. To achieve this aim, common reference characteristics have been defined in order to allow the optimal comparison. The reference power considered for both technologies has been 110 MW and the "power cycle" (turbine, alternator and generator) and the "cooling system" are the same in both configuration. In general terms, the significant differences between both configurations are focused on the area of the solar field, and with it the number of heliostats, and on the storage of thermal energy by inorganic salts. Although it is true that concentrating solar power plant (CSP) in tower without thermal energy storage is not a current commercial configuration, it is very interesting to be able to compare the environmental impacts of both configurations when thermal energy storage is added to the solar plant. In addition, the study ends by assessing whether the environmental impact that is generated by adding thermal energy storage compensates with the improvement of its manageability, its dispatchability and its contribution to decarbonisation.

METHOD: Life cycle assessment (LCA) is a methodology that allows evaluating the environmental loads associated with a product, process or activity, identifying and quantifying the energy, the materials consumed and the waste released into the environment throughout the entire life cycle. The LCA included in this study is carried according to ISO 14040 and 14044. Thus, this LCA is based on the impact assessment method ReCiPe in impact points and GWP in kgCO₂eq and the database used is Ecoivent 3.6, which has positioned itself as a world leader in creating more transparent life cycle impact databases. Moreover, this work encompasses three distinct phases of evaluation: manufacturing, operational, and end of life.

RESULTS AND CONCLUSIONS: At the time of submitting this abstract, the study is on its way.

IMPACT OF PEMFC PERFORMANCE AND DURABILITY ON LIFE CYCLE ENVIRONMENTAL IMPACTS

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INTRODUCTION: There is a big concern regarding environmental impacts in recent years. Paris agreement, which was signed by 195 countries, is another attempt of global action plan to mitigate climate change [1]. In addition EU has very challenging goal to reach carbon neutrality by 2050 [2]. For these and many other reasons, the transition in the energy sector is expected and hydrogen is expected to be one of the key players. [3]. The unique property of hydrogen has made hydrogen Proton-Exchange Membrane Fuel Cell (PEMFC) systems an alternative and complementary solution to conventional power generation systems. Although PEMFC systems are expected to have a lower environmental impact in the operating phase compared to conventional energy conversion systems, there are still significant economic, operational and environmental setbacks. The use of expensive critical materials as platinum or ruthenium in Membrane Electrode Assembly (MEA) has a big influence on economic and environmental parameters. Another technical barrier for the faster penetration of FC is the durability under a wide range of operating conditions [4].

Different organizations (e.g. US Department of Energy) have proposed and published many different methods of accelerate stress tests (AST) to characterize the two key properties of PEMFC systems, which are performance and durability. The objective of testing is to gather enough information about the FC system to understand its performance and/or durability without reaching failure/EoL (End-of-Life). In order to promote the wider use and commercialization of PEMFC systems, targets have been set for the operating lifetime of PEMFC systems to 60,000-90,000 operating hours for stationary PEMFC systems and 5,000 hours (8000 h - long-term target) for systems with dynamic operation (automotive applications). According to the literature a maximum of 10% capacity reduction (voltage potential at nominal operating conditions of the system) according to the Beginning-of-Life (BoL) is defined as EoL and need to be replaced or renewed, [6]. Due to the key degradation processes, which takes place in MEA, efficiency can drop up to 23% [5], and FC stack have to be replaced (EoL), which consequently results in higher costs and bigger environmental impacts of PEMFC systems. Obviously degradation processes influence the efficiency of PEMFC differently in stationary and in dynamic operation regime. Nevertheless that this is evident in researches with experimental approach, the environmental impact assessment using Life cycle Assessment (LCA) approach almost never include the performance degradation during the operating life that contributes to environmental impacts of PEMFC operational phase. Furthermore, there is no operating regime (dynamic, stationary) considered, because dynamic operation accelerates the reduction of the PEMFC remaining useful life (RUL) of the operation, which consequently affects the environmental impact of hydrogen technologies with PEMFC.

METHODOLOGY: For the AST a dynamic load profile that is consistent with the standard tests for dynamic LT PEMFC with a single MEA and based on the New European Driving Cycle (NEDC) profile was used, [7]. This load profile was chosen because it contains all typical operating modes that occur during (dynamic) operation of LT PEMFC systems: Load cycling, on-off, standby, high loads and partial load/rated load operation. Based on chosen AST a semi-empirical model for the PEMFC operating phase was designed, updating the life cycle inventory (LCI) and implementing it in a new, innovative LCA model of the low temperature PEMFC system. Most of the existing LCI for PEMFC operating phase are obtained without degradation affect and operating regime consideration, which was done in this study as additional novelty. Methodology used for environmental impact assessment is LCA methodology according to the ISO

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standards 14040 and 14044, [8], [9], recommended ILCD guidelines [10], and FC-Hyguide, [11]. CML 2001 methodology with 12 indicators was used to assess the environmental impacts of the PEMFC system, [12] and GaBi software was used for LCA modelling, [13].

The novel approach presented in the research is the experimental validation of the AST of LT PEMFC with focus on MEA degradation processes, which allowed us to establish the semi-empirical model of the PEMFC system to determine innovative LCI for LT PEMFC with included operating regime (steady-state/dynamic). The innovative LCI was used in LCA assessment of the PEMFC system and the results were compared with the currently available LCI in Ecoinvent database. For the PEMFC production phase, a new LCA model was created, which allows to change the input material and energy flows.

RESULTS AND CONCLUSIONS:

Results show that degradation processes significantly affect the environmental impacts of the PEMFC system in the production phase and potentially also in the end of life phase due to more frequent replacements of PEMFC system components and shorter life span. This is more evident in the case of 'green' hydrogen (produced from hydro, wind or photovoltaics) use in operating phase. All environmental impacts increase by 51% in the stationary and by 248.9% in the dynamic operating regime in operational phase of PEMFC when using hydrogen from hydroelectricity (EU hydro scenario). In the EU hydro scenario increased hydrogen consumption due to degradation contributes in average 1.5% to the total increase of all environmental indicators, while PEMFC stack replacement contribute as much as 49.5% in stationary and 247.4% in dynamic operating regime to the total average increase of all environmental indicators. In addition energy analysis shown that the efficiency of primary energy invested in the entire life cycle of the LT PEMFC system with 'green' hydrogen use from hydropower is 0.247. With the degradation processes included it decreases to 0.233 for dynamic and 0.236 for stationary operation regime.

ANALYZING DIFFERENT THERMAL MANAGEMENT SYSTEMS FOR Li-ION BATTERY PACK - CFD STUDY

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INTRODUCTION: Lithium ion batteries are the most important component for the electric vehicles. During charging and discharging, the stability and safety of chemicals inside a lithium ion battery are crucial to the working of electric vehicles. Temperature beyond a tolerable range is caused by rapid charging and discharging of the lithium ion batteries. Battery operation and life span is impacted by this expeditious temperature rise. To operate a battery within its safety range, various cooling techniques are introduced. Passive cooling with Phase Change Material is the most effective method because of simple structure and high thermal efficiency. The only disadvantage of PCM is its low thermal conductivity. For a good thermal management system, high thermal conductivity is demanded. Metal foam saturated with Phase Change Material have been focused to investigate the thermal management of lithium ion batteries.

MATERIALS AND METHODOLOGY: This study is focused on the thermal management system needed to enhance the battery pack life span and safety. The aim of the study is to investigate, compare and conclude the best cooling system for lithium ion batteries. The following cooling systems are investigated in our study:

- Air
- Pure Phase Change Material
- Metal Foam Saturated with Phase Change Material

Comparison is done by simulating the battery pack by using computational fluid dynamic software COMSOL Multiphysics 5.5 and results are concluded.

RESULTS : For the case of nickel paraffin foam, it is observed to reach 31% less temperature than natural air circulation. Similarly, the temperature is lowered by 24% by using Pure PCM as compared to natural air circulation. The battery pack temperature behaviors is analyzed at different C-rates.

CONCLUSION : Metal Foam Saturated with PCM has proven the most effective method for cooling of Lithium ion battery pack. Pure Phase Change material has proven less effective due to the low thermal conductivity.

MULTI-SCALE MODELLING OF THE THERMAL RUNAWAY IN Li-ION BATTERIES

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INTRODUCTION: Batteries are one of the key enablers for complying with the Paris Declaration on Climate Change. Batteries are also one of the most widespread energy storage devices and a key component in future energy systems and devices. They are thus enablers for more sustainable mobility and more user-friendly leisure applications, and with the introduction of renewable energy sources, they are gaining significance in energy applications.

This broad range of applications shares certain common high-level objectives, which can be summarized as: higher energy and power density, prolonged life and increased safety of batteries, which will be produced using abundant materials, and which will comply with the principles of circular economy while simultaneously featuring low costs [1]. Additionally, this broad range of applications imposes several application-specific objectives, which cover operating temperatures, specific load profiles, and specific durability and safety criteria. Therefore, a single design cannot optimally fulfil all these requirements. Thus, tailoring battery design to a specific application with the aim of approaching engineering limits presents a significant challenge.

In addition, experimental evidences clearly indicate the importance of the interplay between electric and thermal boundary conditions, cell design and applied materials, side reactions as well as safety implications of batteries, which are not yet captured to a sufficient level by simulations models. As an answer to this challenge, we here present an advanced multi-scale battery modelling framework that can be seamlessly integrated into multi-domain models. Proposed advanced multi-scale modelling framework establishes a consistent link from crystallographic structure of the cathode, over electrode topology, heat generation, and degradation phenomena, to the outbreak of the thermal runaway.

MATERIALS AND METHODS: Methodology is based on the extended governing equations of the advanced multi-scale modelling framework [2] with the aim to establish a consistent link from crystallographic structure of the cathode, over electrode topology, heat generation, and degradation phenomena, to the outbreak of the thermal runaway. Electrochemical and transport equations are inspired by mesoscale transport phenomena and incorporate scale bridging methods to calculate chemical potentials of the primary LiFePO₄ (LFP) particles, formulated on the continuum scale. Degradation models cover mechanisms at the anode, specifically the SEI (solid-electrolyte interphase) formation and SEI decomposition processes, the reaction of intercalated Li with the electrolyte, the deposition of metallic Li, and the calculation of film thickness on the anode particles; degradation of cathode active material; and electrolyte decomposition. The thermal model that matches the level of depth of the electrochemical and the transport model comprises reversible, irreversible and degradation specific heat sources.

To create a challenging virtual test case and to expose the complex interaction of intra-cell phenomena LFP material, characterized by being phase-separating and featuring fast diffusion in one dimension as well as complex mesoscale topology of the secondary particles, is selected as a cathode material. It is paired with the graphite anode. Although demonstrated on LFP-graphite cells, the proposed modelling framework can be applied to other materials by adjusting the inherent material parameters and material specific topological parameters and incorporating other models of main and side reactions.

RESULTS: The basis for the plausible modelling of intra-cell phenomena arises from the proper modelling of transport and electrochemical phenomena, which represents the first part of model validation of the

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advanced multi-scale modelling framework. This validation focuses on phenomena arising from the crystallographic structure specific properties of the LFP cathode material and material specific electrode topology, which influence the electrical and thermal output of the phase separating cathode material.

In addition, results comprise the validation of SEI growth and its impact on battery performance, which forms the basis for further degradation and safety analyses that comprise heat, wait and seek calorimeter analyses. Validated modelling framework was subsequently applied to model outbreak of the thermal runaway during battery cycling. These results confirm the hypothesis that nanoscopic transport phenomena and resulting heat generation decisively influence the entire chain of mechanisms that can lead to the outbreak of the thermal runaway. Results further indicate the importance of plausibly modelling the entire chain of phenomena when assessing these complex yet very realistic use cases. Safety analyses during battery operation are namely decisive for proper selection of cells, their assembly into the modules and packs including selection of the type and topological layout of the cooling concepts as well as development of functionalities of the BMS according to the intended use of the batteries including their duty cycles and ambient conditions.

CONCLUSION: Proposed modelling framework is thus applicable for virtual support of enhanced cell designs with existing materials and for exploring performances and degradation as well as safety relevant phenomena in high fidelity simulation tool capable of interaction with all relevant domains. This enables unprecedented safety analyses in transient operating conditions. This makes it possible to assess the interactions between different domains and optimize domains according to the intended application already very early in the development phase. In addition, spatially resolved results confirm that the proposed modelling framework is capable of supporting not only virtual analyses in the cell design phase but also virtual analyses of the manufacturing process by evaluating the severity of design deviations on transport, electrochemical, degradation, and safety relevant phenomena. Therefore, the proposed methodology significantly contributes to more accurate virtual prototyping, since it enables more efficient frontloading and allows for approaching engineering limits with higher certainty.

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APPLICATIONS OF THERMAL ENERGY STORAGE SYSTEMS FOR NEARLY-ZERO ENERGY DEMONSTRATION BUILDINGS IN CHINA

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INTRODUCTION Nearly-Zero Energy Building (NZEB) is the future building energy efficiency upgrading pathway in China. During China's 13th Five-Year Plan period, China has built more than 10 million m² NZEB in China. The key technical strategies to achieve the energy consumption requirements for NZEB include: 1) reducing energy demand to an extreme low level via passive techniques; 2) improving the energy efficiency of products; and 3) replacing the remaining fossil fuels by various sources of renewable energy. Therefore, to make both renewable and non-renewable energy sources more efficient in NZEB, many of them integrated with energy storage systems. On the basis of existing demonstration projects in China, this study will analysis the common thermal energy storage system used in NZEB and its combination with energy systems.

METHODOLOGIES The study selected 40 built and under construction demonstration projects of nearly zero energy buildings in China. The energy system and energy storage technology of these demonstration projects are analyzed. China has diversity and distinct climatic characteristics. The demonstration projects cover four climatic zones: severe cold, cold, hot summer and cold winter, and hot summer and warm winter, accounting for 60%, 20%, 15% and 5% respectively. Demonstration buildings also include residential buildings (14%), office buildings (10%), comprehensive buildings (7%), hotel buildings (4%) and other conventional buildings, as well as rehabilitation centers (1%) and news centers (1%) and other special function buildings. The demonstration area ranges from 105 square meters to 330,000 square meters. The total area of residential buildings is 594,000 square meters, and the total area of public buildings is totals 181,000 square meters.

The energy consumption of the demonstration project reached the national standard in China "Nearly Zero Energy Building Technical Standard" GB51350-2019. For residential buildings, the heating energy consumption of severe cold and cold buildings is more than 50% lower than the values of the national building energy consumption standard. The annual ventilation, cooling and heating power consumption of residential buildings in hot summer and cold winter areas is less than 15kWh/m²a. Compared with the national building energy efficiency standards, the energy consumption of demonstration buildings in hot summer and warm winter reduced by more than 30%. For public buildings, the actual energy consumption is more than 50% lower than the national building energy standard.

RESULTS Among the 40 demonstration buildings, a total of 9 projects have adopted heat storage technology, 7 projects are equipped with water storage tanks, of which 4 buildings are equipped with solar energy-ground source heat pump-water storage system, and they are all public buildings. It can be seen that this system is the most common heating system and energy storage technology for nearly zero energy buildings in China.

The combination of solar energy and GSHP is very complementary, which can effectively reduce installed capacity, reduce the length of buried pipe long, reduce initial investment, and improve system efficiency (Buker and Riffat, 2016). At present, there have been a large number of studies on the design, optimized operation, energy consumption characteristics and other aspects of solar energy and ground source heat pump energy storage systems.

The system is suitable for areas where the demand for cooling and heating does not match. By optimizing the operation mode, energy consumption can be effectively reduced, and system efficiency improved (Li et al., 2018). For all applications in the demonstration projects, the heat absorbed by the solar collector is used for heating. The heating operation mode of the system can be divided into four types: 1) the ground source heat pump operates alone; 2) the solar hot water storage tank system alone provides heating for the building; 3) the ground source heat pump operates intermittently. When the heat pump stops working, the heat from solar transfers to the soil for storage; 4) The energy in the water storage tank and in the soil together provide heat for the heat pump. The two parts of heat are connected in parallel or in series with the heat pump (Dai et al., 2015; Kjellsson et al., 2010).

CONCLUSIONS Through the analysis of 40 nearly zero energy buildings, it can be seen that 23% projects adopt heat storage technology. Solar energy-ground-source heat pump-water storage system is the most common form of energy storage applications in nearly zero energy buildings in China.

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DEVELOPMENT AND DEMONSTRATION OF A ZERO-ENERGY-SAUNA

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INTRODUCTION: The energy transition from fossil to renewable energy requires the integration of energy storage. While the public debate focuses mainly on electrical energy storage, the analysis of the total energy consumption reveals that a large share of energy is finally consumed in the form of thermal energy. Furthermore, in the personal perception, the energy transition is often associated with a required reduction of energy consumption and thus with a reduction of the living standard. However, from a technical point of view, it can be possible to maintain our standard of living while achieving the goals of the energy transition. Against this background, the presented research project addresses a wellness and comfort product with a high energy demand: the sauna. The aim of the project is to develop and demonstrate a so-called Zero-Energy-Sauna. In general, a Zero-Energy-Sauna is a sauna, which fully covers its energy demand through locally available renewable energy sources.

MATERIALS AND METHODS: In a preliminary study, various concepts have been systematically derived and assessed. One innovative concept has been patented and was implemented in the presented research project. The implemented concept adopts solar energy and applies two types of thermal energy storage: a pressurized, stratified hot water storage and a closed low-pressure adsorption storage. The main purpose of the hot water storage is to provide heat, while the purpose of the adsorption storage is to provide steam. In a first step, simulation models of the two thermal energy storage were developed. The model of the hot water storage considers the effect of natural convection, which is especially important when hot water is injected into the storage at a height of lower temperature. For the adsorption storage, a previously developed and published model was adopted. The model was extended by internal heat exchanger fins and a metal lid. Based on these models, different charging and discharging scenarios as well as different designs of the thermal energy storages were examined by means of numerical simulation. The derived optimum designs provided the blueprints for the thermal energy storages integrated in the Zero-Energy-Sauna. Subsequently, the Zero-Energy-Sauna was constructed and extensive experimental studies were conducted over several months during winter to investigate the behavior of the two thermal energy storages and to evaluate the overall performance of the Zero-Energy-Sauna under practical conditions.

RESULTS: The experimental studies continuously covered the repeated charging and discharging cycles of the thermal energy storages. During the charging phase, the charging power from the solar thermal collectors as well as the photovoltaic modules was monitored and the charging state of the two thermal energy storages was determined by measuring temperature distribution, pressure and water load. During discharging, the temperature distribution in the sauna room as well as the humidity were measured, while continuing the measurement of the charging state of the thermal energy storages.

CONCLUSION: The experimental results validate the predictions of the numerical simulations and demonstrate the successful operation of the realized Zero-Energy-Sauna.

DEVELOPING NORTHERN GREENHOUSES : AN EXPERIMENTAL AND NUMERICAL STUDIES

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INTRODUCTION: Due to the difficult access to their territories, Northern Canada's Inuit have faced major adaptation challenges in recent decades, notably in terms of food and energy [1]. This research focuses on the potential of greenhouses in the circumpolar territories in order to meet the challenges of local supply and adaptation of the food system. The territories targeted for this research are located in the Canadian Arctic, primarily in Nunavik, which is the northern Inuit territory located in the province of Quebec.

MATERIALS AND METHODS: The Kuujuaq cooperative greenhouse is a modified arch greenhouse built in 2012, made of polycarbonate, with a ground area of 140 m². It is a passive structure, meaning that it is neither heated nor cooled. However, there is an automatic ventilation system which is triggered when a predetermined temperature is exceeded to prevent extreme heat inside the greenhouse.

This greenhouse was instrumented in June 2016 to collect temperature and relative humidity data throughout the growing season. In addition to monitoring the outdoor conditions, a dozen of probes have been placed at different heights and positions in order to assess the thermal gradients within the space. Two pyranometers are installed to measure the incident solar flux on the walls and the related absorption coefficient. The analysis of the collected data highlighted several design problems. For instance, low thermal inertia causes very high difference in temperature between day- and nighttime within the greenhouse. To overcome this problem a sensible thermal energy storage system (TES) has been designed, built and installed in the greenhouse [2].

This TES includes two sub-systems: one passive and one active. The passive system consists of a concrete slab in the middle of the greenhouse and rocks in gabions surrounding the culture area. The active system allows automated circulation of air in a bed of local rocks (40 103 kg) which is located under the culture area. These sub-systems have low environmental impact as well as simplified maintenance.

This system provides reasonable results (COP between 1.4 and 3); however, major improvements can be envisioned to increase its efficiency in order to regulate the temperature in the greenhouse during the day but also to extend the growing season (which is currently barely 4 months long). A numerical model of the TES based on the Modelica Library has been used to evaluate these options [3]. It is intended to integrate this numerical model to a more general model of the greenhouse using hypotheses that provide acceptable calculation times such as that the rocks are small enough to be considered as thin bodies ($Bi \ll 1$).

RESULTS AND CONCLUSION: The analysis of the measurements carried out over two periods, before / after the installation of the storage system, with a similar meteorology (temperature and solar resource) shows for example a decrease from 30 to 24°C of the maximum temperature in the middle of the day, and an increase of the minimum temperature at night from 5°C (without the storage system) to 12°C (with). These two effects are favorable to crop growth. The comparison of the experimental and numerical results with and without the storage system allowed us to calibrate and validate our model. A parametric study was then carried out in order to determine the most appropriate control parameters (air mass flow, thresholds of the control system, ...). Finally, and in order to extend the growing season, the coupling with a solar thermal system with air as the heat transfer fluid has been estimated.

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THERMOCHEMICAL HEAT STORAGE THROUGH CaO-MAYENITE/CaCO₃ SYSTEM: THERMAL PERFORMANCES COMPARISON FOR TWO SYNTHESIS METHODS

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INTRODUCTION: CaO-based materials using mayenite (Ca₁₂Al₁₄O₃₃) as inert matrix have been previously developed and proposed for CO₂ capture applications through calcium looping processes [1,2]. These systems are very promising also for thermochemical storage (TCS) purposes [3,4], mainly thanks to their high reaction enthalpy, according to the reversible gas-solid reaction: CaO(s)+CO₂(g) -->CaCO₃(s) + 178 kJ/mol. In the TCS framework, several aspects regarding the CaO/mayenite systems have to be further investigated, such as thermal properties and actual storage density [5]. Generally, these properties depend on the adopted synthesis method [6]. The present work aims to assess the effect of two different preparation methods, namely a one-step sol-gel method (sample A) and a two-step impregnation method (sample B), on the thermophysical properties of a mayenite-supported CaO/CaCO₃ material, in view of its application in TCS systems. At this purpose, different samples of CaO/mayenite powder were analysed to determine relevant properties such as heat capacity, reaction enthalpy, thermal conductivity and maximum attainable conversion. The obtained results were compared to select the best synthesis method.

MATERIALS AND METHODS: As described in a previous work [9], different CaO/mayenite (75/25 % w/w) samples were synthesized by ENEA through two different methods. The first one consisted of 1 step-sol-gel method [7] (sample A). The second method consisted of a 2 steps preparation route (sample B). In the initial step, CaO and Al(NO₃)₃·9H₂O were mixed in the stoichiometric ratio to obtain 12CaO-7Al₂O₃, i.e the mayenite matrix, with the sol-gel method procedure. In the subsequent step, the CaO active phase was wet-impregnated over the obtained mayenite. CaO and mayenite were then mixed with a deionized water/2-propanol solution and stirred, with a CaO content of 75 (% w/w). The suspension was heated at 80°C and the sample was air calcined at 1000°C [8].

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed in a TGA/DSC1 Mettler Toledo Analyser over samples A and B in N₂ atmosphere (40mL/min) placed in alumina crucibles (70 µL). In particular, carbonation and decarbonisation enthalpies were determined using different metals as external standard reference materials, namely indium, zinc, aluminum and silver (Mettler Toledo procedure). The charging/discharging time evaluation allowed to calculate the related heat fluxes. Moreover, the TGA apparatus was also employed to determine the specific heat of the decarbonated samples (CaO/mayenite) by using a DIN 51007 protocol, based on the comparison of the sample heat flux with the one presented by pure sapphire (NIST).

To measure the heat capacity of pure mayenite and the carbonated samples, a DSC equipment (DSC1 Mettler Toledo) was employed according to the DIN 51007 standard method. Thermal conductivity of samples A, B and pure mayenite was determined up to 200°C with Hot Disk TPS 2500.

TGA carbonation conversion was determined according to the following temperature program: the sample was heated up to 900°C at 50°C/min in N₂ atmosphere (gas flow of 50ml/min), then an isothermal step of 1 h was carried out at 900°C to allow complete sample dehydration and de-carbonation, and finally isothermal carbonation under pure CO₂ flow for 8 h was conducted.

RESULTS: For both samples A and B the decarbonisation step in TGA was always performed at 900°C, while the carbonation reaction, the slowest step [6], was performed at a temperature of 700°C. In isothermal

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conditions, for longer times-on-stream, sample B achieved a higher carbonation conversion (95% w/w) than sample A (84% w/w); however, independently from the preparation method adopted, appreciable conversions are attained. The observed differences in the thermophysical properties of the two samples can be related to the different preparation procedures. It could be suggested that sample B offers an enhanced available surface area for CO₂ absorption related to its more porous texture, as previously discussed [9].

CONCLUSIONS: The preparation method significantly affects the conversion of the carbonation reaction and the best response comes from impregnation method, as sample B shows a higher carbonation conversion and more performing thermophysical properties.

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CYCLIC CO₂ HYDRATE-BASED COLD THERMAL STORAGE AND CO₂ GAS STORAGE ENABLED BY AMINE INFUSED HYDROGELS

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Cold thermal energy storage (CTES) has been implemented for various cooling systems. CO₂ hydrate manifests superior properties compared to other phase change materials, including large storage density, suitable phase change temperature and low material cost. However, a usually neglected key point of CO₂ hydrate-based CTES applications is that, CO₂ gas is released from hydrate when it is dissociated, and a gas storage is a must in the system to temporarily store released CO₂ gas in a considerable amount for cyclic gas hydrate formation and dissociation. Suitable CO₂ sorbents to reduce gas storage capital and operational cost are needed before any CO₂ gas hydrate-based CTES can be prototyped. This work studies the absorption and regeneration performance of a new amine-functionalised CO₂ sorbent, amine infused hydrogels (AIHs) under various operating conditions, and provides an experimental study on the viability of the AIH-enabled CO₂ gas storage to assist in the cyclic operation of a CO₂ hydrate-based CTES system. A small-scale laboratory demonstration with a hydrate-based CTES and an AIH-filled gas storage was developed with the temperature and pressure recorded. The synergistic and alternative operation of CO₂ gas regeneration–CO₂ hydrate formation and CO₂ hydrate dissociation–CO₂ gas adsorption were conducted to evaluate the system performance. It was found that increasing the pressure and decreasing the temperature to some extent enhanced the absorption of CO₂. Temperature was a main driving factor of CO₂ regeneration performance and 110°C was found the optimal regeneration temperature. The AIH showed no obvious recession in the first three cycles of absorption and regeneration. The main result shows that the recession of AIH should be considered in the design which may be caused by amine and water evaporation.

VALORIZATION OF RED MUD AS A SUPPORTING MATERIAL FOR MEDIUM-HIGH TEMPERATURE THERMAL ENERGY STORAGE.

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INTRODUCTION: Aluminum is the second most produced metal in the world, after stainless steel, with considerable presence in several important industrial sectors such as aerospace, automobile and electrical distribution. Its production is an energy-intensive process which accounts for ~0.5 Gt of CO₂ emissions/year¹. Identifying solutions to lower energy consumption can both decrease its production costs and GHG emissions. Thermal energy storage (TES) is a cost-effective solution that can help address thermal management challenges.

Red mud (RM) is an industrial waste of the aluminum industry with a 150 Mt/year worldwide production². Its disposal is facilitated typically in dykes/dams or alternatively directly in the sea posing a considerable environmental impact due to its high alkalinity 11.3 ± 1 and traces of heavy metals¹. To this end researchers have been trying to identify pathways to transform this industrial waste into a by-product, but despite efforts, present worldwide utilization rate is only 15%³.

RM constitutes primarily of a mixture of ceramic oxides, making it an ideal skeleton material for a composite phase change material (CPCM). By using a PCM with a medium temperature melting point, such as molten nitrate salts, a CPCM can be used to store waste heat from medium-high temperature streams. To this end in this work, a novel RM-molten salt composite is presented and its thermal performance as well as thermal stability is assessed.

MATERIALS AND METHODS: The Solar salt (SS, 60-40 wt.% NaNO₂ and KNO₃) is the PCM material used in this study, purchased from Sigma Aldrich (purity >99%) and prepared through a static melting method⁴. The supporting CPCM material is the RM obtained from the company "Aluminium of Greece" and is heated to 500 °C (15h) to remove the majority of H₂O (~26 wt.%) RM and SS grains are mixed, at 0.7:0.3 to 0.4:0.6 mass ratios, milled in a ceramic mortar and then mixed to produce a homogenous mixture, which is then compressed at 100 MPa for 2mins in a 13mm die that is subsequently heated to 400 °C at 5 °C /min and then cooled. Chemical and phase composition is assessed using a Bruker D8 Advance XRD X-Ray Diffraction (XRD) with a 2°/min step at room temperature in air. Melting point, latent heat, and specific heat capacity are assessed through Differential Scanning Calorimetry (DSC) on a DSC2 Mettler Toledo under air atmosphere, from 20 to 400 °C with a heating rate of 10 °C /min, in aluminium crucibles and according to DIN51007 (sapphire method). Thermal diffusivity and conductivity are obtained through the Laser Flash Technique (LFA 427 device, Netzsch). Finally, the density of the samples is assessed using a helium pycnometer (Accupyc II 1340, Micromeritics).

RESULTS: A total number of 48 cycles are conducted to assess the thermal stability of the material. XRD measurements before and after cycling denote perfect chemical compatibility between the two materials. Latent heat and melting point are found to be stable after 48 cycles. Addition of SS reduces the porosity and increases the density of the CPCM. The latter is found to slightly increase after 12 cycles and then remains stable.

Solid phase specific heat capacity of the CPCMs is found to be ranging on average from 0.92 J/g °C for RM to 1.28 J/g °C for a 0.6:0.4 RM-SS ratio in a temperature range of 25 to 250 °C. In the liquid state the optimal average C_p is obtained for the latter composition at 1.35 J/g °C, while bulk RM is measured to be 1.17 J/g °C. C_p is found to increase linearly in terms of temperature independent of composition, with attaining maximum value around the SS melting point (220 °C). Maximum latent heat is measured to be 58 ± 4 J/g for a 60% SS content. SS content increases both thermal diffusivity and conductivity. A large increase is noted after 12 cycles (34.5%), while values remain stable throughout the remaining cycles. For RM, after 48 cycles, it is measured to be 0.213 mm²/s and reaches a maximum of 0.554 mm²/s for 40% at 25 °C. Similarly, optimal average thermal conductivity is obtained at 40% SS with a value of 0.83 W/mK, while the RM thermal conductivity is measured to be 0.306 W/mK in the operating temperature range. In terms of temperature both properties are found to be decreasing up to 200 °C and then demonstrating fairly stable values up to 400 °C for CPCMs. RM thermal conductivity appears to remain stable with temperature within the range of propagated uncertainty throughout the measured temperature range. Energy storage density is calculated for temperature ranges of 25 to 250, 300 and 450 °C. Addition of SS in the compressed RM leads to an increase in the energy density, with a maximum of 1396 MJ/m³ obtained for a temperature range of 25 to 400 °C.

CONCLUSION: To summarize a novel CPCM consisting of RM and SS is presented. Its thermal stability, thermal properties and energy density are found to be excellent. Combined with the associated low material and setup costs, the proposed application is ideal for the valorization of the RM as a by-product for thermal energy storage/waste heat recovery applications in medium-high temperature energy intensive industries with relative heat streams.

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POTENTIAL NEW REFERENCE MATERIALS FOR CALORIC MEASUREMENTS ON PCM

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INTRODUCTION: Current applications of PCM focus on the temperature range of about -40 °C to +80 °C, with interest up to about 400 °C. For the determination of the heat stored as a function of temperature by calorimetric measurements a variety of methods and instruments exist, some recently developed to characterize larger samples with volume of up to 100 ml. Reference materials for temperature and amounts of heat are needed for calibration, testing, as well as for relative / comparative measurements. Reference materials for temperature refer to a phase change temperature T_{cp} , for heat to a phase change enthalpy $\Delta_{cp}h$ or heat capacity of solids and liquids. Reference materials being certified, meaning established as standard, are for T_{cp} and $\Delta_{cp}h$ e.g. the metals mercury, gallium, and indium, as well as other materials like cyclohexane, biphenyl, and naphthalene. Water is only certified for T_{cp} . This choice is insufficient for the required temperature range, and especially for large samples size. Large amounts of mercury are dangerous; the other materials are expensive in the required high purity. For convenience, often materials where data are found in literature are used, for example octadecane. A review for octadecane (Faden et al. 2019) however shows that literature data range for the melting temperature from 298.5 K to 303.7 K, and for the melting enthalpy even from about 200 J/g to 260 J/g. This is insufficient, and therefore the use of just some material is highly risky and not recommended. In a recent publication (Mehling et al. 2021) an extensive introduction, review, and recommendations for new reference materials for calibration and testing were given. As critical were identified the purity of a sample, the accuracy of a measurement, and last but not least what exactly a value given refers to. For example, for the phase change temperature the onset, peak, as well as offset temperature are used. For T_{cp} and $\Delta_{cp}h$ the recommendations made comprise water at 0 °C, and as options the n-alkanes dodecane at -10 °C, tetradecane at 6 °C, hexadecane at 18 °C, and octadecane at 28 °C. At higher temperatures, alkanes are no good candidates, at least if considering high purity to have a well-defined composition. The work presented here focuses on applying these results, and their consequences.

MATERIALS AND METHODS: There are two ways to approach the problem of a lack of reference materials for temperature and amounts of heat, needed for calibration, testing, and also for relative / comparative measurements. The easy way is to take a suitable material, buy a larger amount possibly even of low purity because of the price, and then measure the desired property with high accuracy on a sample. If the large amount has been homogenized sufficiently, a large number of further samples for calibration and testing can be taken. The common way of establishing reference materials is to find generally suitable materials, and then measure the desired property with high accuracy on very pure samples. The high purity is needed to assure that new samples are available of the material with same composition, anywhere and anytime. In the work presented here, alkanes and water are investigated, by own measurements and literature data, and discussed. The work presented focuses, where good candidates for reference materials are available, on showing how purity of a sample, the accuracy of a measurement, and what exactly a value refers to, effect values, with a focus on water and the alkanes. Where good candidates are missing, the gap can be closed using samples with lower, but well known purity, taken from a single larger batch.

RESULTS: Water can be used as reference material also for $\Delta_{cp}h$. The sufficient purity is easily available, values from highly accurate measurements are available, and due to the sharp phase change at 0 °C what

ENERSTOCK 2021

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the value refers to is well-defined. However, for example measurements using DSC give a peak of significant width, due to the heating rate, so comparison with reference data must be done carefully. From the alkanes, dodecane C12, tetradecane C14, hexadecane C16, and octadecane C18 are suitable, covering the range -10 °C to 28 °C. They have a single phase transition, and are available in high purity for reasonable price. However, they do not have sharp phase change temperatures such that what values refer to is critical. And literature values with high accuracy are still rare for most of them. At higher temperatures, price and phase transition behavior are a problem. Then the approach of characterizing a sample from a larger amount of less pure and thus cheaper material can be followed. This approach is applied by the RAL Quality Association PCM (<https://www.pcm-ral.org/pcm/en/>).

CONCLUSION: For calorimetric measurements on PCM there is a lack of reference materials. Using just other materials and literature data, with unknown accuracy of the values and purity of the material, is not recommended. Potential new reference materials are found among the alkanes up to about 30 °C. For high temperatures, samples from a well characterized larger batch can be an option. In addition, water at 0 °C can be recommended not only for T_{cp} , but also for $\Delta_{cp}h$. Generally, as measurement parameters of calorimetric methods affect the shape of the resulting $h(T)$ curves, e.g. measurements using DSC give a peak of significant width even for water, due to the heating rate, comparison with reference data must be done carefully.

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ENERSTOCK 2021

AUTHOR INDEX

ENERSTOCK 2021

A

Abdi Amir, 61, 139
 Abokersh Mohamed, 254
 Abuasbeh Mohammad, 210, 211
 Acuna Jose, 210, 211
 Agrawal Nidhi, 108
 Aguilar Teresa, 90, 259
 Ahlkrona Malva, 211
 Ahmad Abrar, 147
 Ahmed Ayaz, 270
 Al Koussa Jad, 203
 Alawadhi Ayesah, 91
 Alcántara Rodrigo, 259
 Almendros-Ibáñez José Antonio, 128, 184, 202
 Alvaro Fabrizio, 157, 160
 Anagnostopoulos Argyrios, 281
 Aranzabe Estibaliz, 158
 Aristov Yuri, 25
 Arrabie Cedric, 276
 Arribalzaga Peru, 150
 Avila Aina, 169
 Azad Mohammad, 214

B

Bach Andreas, 238
 Badenes B. Borja, 40
 Bantová Sylva, 229
 Bardy Dylan, 93, 174
 Barmparitsas Nikolaos, 187, 194
 Barreneche Camila, 73, 99, 100, 102, 161, 222, 231, 248, 257
 Basta Vit, 39, 112
 Bastin Larsen Chris-André, 84
 Bathen Mina, 84
 Bauer Dan, 38, 114, 125, 241, 250, 263
 Bauer Thomas, 165, 185, 241
 Bayón Rocío, 58
 Bédécarrats Jean-Pierre, 178
 Bele Marjan, 48
 Belik Sergej, 146
 Belmonte Juan Francisco, 128, 202
 Bentivoglio Fabrice, 55
 Bernardi Adriana, 121
 Bernehed Aiko, 130
 Bielsa Daniel, 150
 Biramo Yifru Woldemariam, 243
 Blanchard Didier, 88
 Boer Dieter, 113, 256
 Bokhoven Teun, 1
 Bonanno Antonino, 185, 194
 Bonk Alexander, 165, 185
 Boquera Laura, 106
 Borri Emiliano, 11, 115, 138, 157, 193
 Bou-Zeid Elie, 151
 Boyer Séverine, 220
 Brancato Vincenza, 25, 31
 Brideau Sébastien, 174
 Bruch Arnaud, 27

Brüggemann Dieter, 75, 208
 Brütting Michael, 149
 Bürger Inga, 33
 Byrne Ciara, 23

C

Cabeza Luisa F., 11, 106, 115, 118, 126, 138, 175, 184, 187, 193, 194, 209, 256, 267
 Calabrese Luigi, 31, 92, 157
 Calderón Alejandro, 73, 161, 248
 Camacho Iker, 163
 Campos-Celador Álvaro, 178
 Capri Angela, 25
 Carrillo-Berdugo Iván, 246, 259
 Castro J. Ramon, 104
 Chàfer Marta, 126, 175
 Chaudhari Ojas Arun, 39
 Chen Bao, 154
 Chiu Justin NW, 63, 69, 132, 139
 Choi Wonjun, 141
 Colladon Andrea Fronzetti, 171
 Córcoles Juan Ignacio, 128
 Coronado Juan M., 153
 Corsaro Natale, 278
 Cosquillo Mejia Aldo, 22
 Crespo Alicia, 115, 118
 Cuevas C. José M., 39

D

Dahash Abdulrahman, 17, 191, 196
 Daschner Robert, 66
 Dauvergne Jean-Luc, 56, 90, 175, 205, 261
 D'Avignon K., 184
 Dawoud Belal, 25, 193
 De Carli Michele, 121
 de Gracia Alvaro, 115, 118
 Deinert Lisa, 66
 Delgado Monica, 139, 220
 Dengel Andreas J., 250
 Diarce Belloso Gonzalo, 68, 139, 178, 208
 Díaz Minerva, 116, 128, 184
 Ding Yulong, 71, 98, 102, 152, 169, 222, 257, 261, 280
 Dino Giuseppe, 187, 194
 Diriken Jan, 203
 Djebbar Reda, 93, 174
 Djinović Petar, 14
 Dmitruk A., 189
 Domingo J., 189
 Dominko Robert, 143
 Donaldson Adam, 214
 Doppiu Stefania, 90, 158, 264
 Dovjak Mateja, 65, 182
 Drueck Harald, 78

ENERSTOCK 2021

E

Earon Robert, 211
 Ebert Hans-Peter, 149
 Edel Karin, 104
 Edén Ted, 243
 Egea A., 43
 El Mankibi Mohamed, 182
 Emir Sedat, 217, 226, 234
 Engelbrecht Kurt, 36, 129
 Englmaier Gerald, 139
 Enríquez J., 189

F

Fabiani Claudia, 159, 171
 Faden Moritz, 206
 Faik Abdessamad, 158, 261
 Falco Marisa, 9, 52
 Fan Guangyao, 109
 Felbinger Jonina, 33
 Ferguson Alex, 174
 Fernández A. Inés, 73, 161, 222, 231, 248
 Fernández Ángel, 106
 Fernandez Cesar, 118
 Fischer Fabian, 30
 Fiß Michael, 123, 250
 Fluri Thomas, 105
 Fontana Patrick, 39
 Fraisse Gilles, 215
 Franquet Erwin, 215
 Frazzica Andrea, 25, 31, 92, 116, 187, 194
 Fujii Shoma, 62
 Fumey Fumey Benjamin, 7
 Funayama Shigehiko, 86
 Furbo Simon, 139

G

Gaberšček Miran, 47
 Gagnière Emilie, 55
 Gaidajis Georgios, 281
 Galgaro Antonio, 121
 Gamallo Pablo, 248
 Gamisch Sebastian, 50, 139
 García A., 43
 García Ane Miren, 150
 García-Romero Ana, 68, 178
 Gasa Gemma, 267
 Gauthier Geoffroy, 196
 Gengembre Edouard, 154
 Gerbaldi Claudio, 9, 48, 52
 Geyer Michael, 241
 Giacomello Alberto, 261
 Gibout Stéphane, 215, 276
 Giuliani Genia, 191
 Giuliano Stefano, 241
 Gleißl Jakob, 208
 Glorieux Christ, 283

Göktepe Bayan Gizem Biçer, 217, 226, 234
 Golobič Amalija, 97
 Gómez M., 189
 Gonçalves Soares Ana, 203
 González-Fernández Luis, 163
 Gordeeva Larisa, 25
 Göschel Thomas, 127
 Grabmann Michael, 42
 Grau-Crespo Ricardo, 246
 Griesbach Marco, 75
 Grosu Yaroslav, 163, 261
 Groulx Dominic, 139, 181, 214
 Grysan Patrick, 48
 Gschwander Stefan, 7, 50, 139, 183, 228
 Gunasekara Saman Nimali, 88, 243
 Güngör Özge, 217, 226, 234
 Guo Jiacheng, 109
 Gutierrez Andrea, 37, 263

H

Hogg EW. LuVerne, 93
 Hafner Bernd, 78
 Haile Sossina M., 155
 Haillet Didier, 276
 Harada Takuya, 86, 144
 Hauer Andreas, 4, 7, 30
 Haussmann Thomas, 183, 224
 Hendry Reto, 199
 Hensel Stefan, 78
 Herbringer Florent, 139, 181
 Hernáiz Marta, 158
 Herrero Ruth, 43, 189
 Hiebler Stefan, 54, 221, 233
 Hien Wong Nyuk, 175
 Hodnik Nejc, 47
 Hoffschmidt Bernhrd, 241
 Hofman Martin, 38, 112
 Hühlein Stephan, 139
 Höllebauer Andreas, 42
 Holmberg Henrik, 119
 Hoock Peter, 54, 221, 233
 Horgnies Matthieu, 154
 Hrdlička František, 38, 104
 Humbert Gabriele, 71

I

Igartua Josu, 90
 Ikeda Shintaro, 141
 Issayan Gayaneh, 95
 Ivanjko Štefan, 173

J

Jiménez-Esteller Laureano, 113
 Jockenhöfer Henning, 125
 Johannes Kevyn, 27, 154
 Johnson Maike, 125, 250

ENERSTOCK 2021

Jovanovič Primož, 47
Juschka Winfried, 78

K

Kackmar J., 189
Kaneko Junko, 86
Kanematsu Yuichiro, 62
Karabanova Anastasiia, 88
Kardaş Gülfeza, 147, 217, 226, 234
Karellas Sotirios, 187, 194
Kargl Florian, 60, 180, 219
Kato Yukitaka, 86, 144
Katrašnik Tomaž, 271
Kawaguchi Takahiro, 212
Kerskes Henner, 19
Khliyev Nikita, 123
Khliyeva Olga, 123
Kick Moritz, 228
Kikuchi Yasunori, 62
Kirincic Mateo, 82
Kirk Caroline, 57
Klasing Freerk, 185
Klinker Felix, 149
Klobčar Damjan, 207, 251
Klünder Franziska, 224
Knabl Samuel, 21
Knobloch Kai, 36, 129
Koçak Burcu, 253
Kok Skov Christian, 16, 196
Kolar Peter, 207, 251
Kolesnik Lindgren Julian, 211
Koll Gerrit, 241
Köll Rebekka, 21, 72
König-Haagen Andreas, 75, 139, 208
Kota Manikantan, 108
Kouchachvili Lia, 93
Koželj Rok, 65, 80, 207, 251
Kraft Werner, 81, 85, 219, 255
Krimmel Stefan, 32
Kroll Ullrich, 198
Kühl Lars, 137
Kümpel Alexander, 137
Kurniawan Ade, 212
Kuznik Frédéric, 27, 154
Kvalsvik Karoline, 119
Kweke Tchana Telesphore, 105

L

La Mazza Emanuele, 157, 160
Laevemann Eberhard, 77
Lager Daniel, 7, 53
Lanchi Michela, 278
Lannazzo Daniela, 160
Lanza Maurizio, 157
Largiller Grégory, 27, 55
Larrinaga Pello, 68, 178
Lazaro Ana, 7, 139, 220
Lazzarotto Alberto, 210

Leang Enghok, 215
Lee Doyun, 141, 200
Lenic Kristian, 82
Leontaritis Aris, 187, 194
Leusbrock Ingo, 7, 153
Leys Jan, 283
Liberatore Rafaele, 236, 265, 278
Linder Marc, 22, 33
Lingua Gabriele, 9, 48
Liu Changping, 273
Liu Zhijian, 109
Llantoy Noelia, 126
López Gabriel Alejandro, 264
Lorber Kristijan, 14
Lotrič Andrej, 268
Lott Stefanie, 78
Louis Piquard, 55
Lund Henrik, 5, 129
Lunnon-Collery Adam, 110

M

Magin Denis, 55
Magni Mara, 176
Mahroug Imane, 90
Majo Marc, 161, 231
Mal Suzana, 29, 97
Mands Erich, 137
Manente Giovanni, 152
Manna Carlo, 203
Mansi Emiliana, 278
Maranda Simon, 238
Marinova Nevena, 264
Markides Christos, 136
Martin Viktoria, 63, 88
Martínez Mònica, 167
Mastronardo Emanuela, 155
Matsuda Yuki, 141, 200
Mazaj Matjaž, 23
Mehling Harald, 283
Mele Igor, 271
Meligrana Giuseppina, 9
Meloni Simone, 261
Mesquita Lucio, 174
Midttømme Kirsti, 41, 119
Mikhaeil Makram, 25
Miliozzi Adio, 236, 265,
Milone Candida, 31, 157, 160
Mizukami Hikaru, 144
Mlakar Nejc, 268
Mlakar Urška, 46, 80, 239
Monfet Danielle, 276
Monokrousou Europe, 187, 194
Mori Mitja, 268
Morin Vincent, 154
Moser Maria, 7
Mselle Boniface Dominick, 115, 138, 187, 209
Mücke Jan Markus, 198
Muhammad Yousif, 36, 129, 270
Müller Adrian, 238

ENERSTOCK 2021

Müller Dirk, 137
 Müller Lukas, 238
 Müller Ralf, 105
 Muñoz J., 189
 Mura Ernesto, 169
 Muser Christoph, 7

N

Næss Erling, 84
 Nakagaki Takao, 62
 Naplocha K., 189
 Navarro Antonia, 106
 Navarro Helena, 98, 102, 169, 257
 Navarro M. Elena, 222
 Navarro Maria Helena, 281
 Navarro Miguel, 220
 Navas Javier, 246, 259
 Nees Frank, 81, 85, 219, 255
 Nefodov Dimitri, 34, 117
 Nejad Ghafar Ali, 39
 Nicolini Daniele, 236, 265
 Nikulin Artem, 56, 123, 205, 261
 Nitsch Birgo, 187, 194
 Nitsche David, 42
 Nomura Takahiro, 212
 Novotny Vaclav, 38, 112
 Nyholm Humire Emma, 269

O

Obergfell Tabea, 183
 Obrecht Christian, 154
 Ochs Fabian, 7, 17, 176, 191, 196
 Ocvirik Manca, 29
 Odenthal Christian, 185
 O'Donovan Keith, 72, 153, 196
 Olofsson Bo Bo, 211
 Ooka Ryoza, 141, 200
 Ortega-Fernández Iñigo, 150
 Ortuondo Asier, 205
 Osterman Eneja, 195
 Ostrý Milan, 229

P

Padilla José Antonio, 167
 Paksoy Halime, 12, 147, 217, 226, 234, 253
 Palacios Trujillo Anabel, 98, 102, 169, 222, 257
 Palamara Davide, 92
 Palm Björn, 210, 211
 Palomba Valeria, 92, 116, 187, 194
 Palomo del Barrio Elena, 56, 90, 123, 158, 163, 177, 261, 264
 Palumbo Mariana, 113
 Parramon Jordi Sancho, 14
 Patil Ajinkya, 139, 181
 Peham Lukas, 42
 Peña-Cordero Manuel, 259
 Pérez J., 43

Petek Urša, 47
 Peuvrel-Disdier Edith, 220
 Piche Paul, 276
 Pilař Lukáš, 104
 Piperopoulos Elpida, 31, 157, 160
 Pires Bjørgen Karl Oskar, 134
 Pisello Anna Laura, 106, 151, 171, 175
 Platzer Bernd, 198
 Pockelé Luc, 121
 Pöllinger Simon, 139, 233
 Portilla Yasmina, 158
 Potamitis Christos, 239
 Pressl Dieter, 77
 Prieto Cristina, 267
 Proverbio Edoardo, 31, 92
 Pugstaller Robert, 42
 Pulham Colin R., 57

Q

Qian Xin, 155
 Qiao Geng, 169
 Quant Colón Laura, 68, 178

R

Ramstad Randi, 119
 Rangel Correa Ferreira Igor, 27
 Rathan Miroslav, 38, 112
 Rathgeber Christoph, 7, 30, 139, 221
 Ravotti Rebecca, 57
 Rawson Anthony, 60, 180, 219
 Reisenbichler Michael, 196
 Renn Steffen, 137
 Richter Markus, 34, 117
 Riedel Uwe, 241
 Ristić Alenka, 2, 7, 23, 29, 80, 97
 Rodman Oprešnik Samuel, 173
 Rojas Esther, 58
 Rojo Hurtado Ander, 68
 Rougé Sylvie, 27
 Ruiz-Zepeda Francisco, 47

S

Shaplov Alexander S, 48
 Saffirio Sofia, 9, 52
 Şahan Nurten, 217, 226, 234
 Sajot Edgar, 276
 Sakai Hiroki, 212
 Salgado-Pizarro Rebeca, 73, 100, 222, 231
 Sanner Burkhard, 39, 121, 137
 Santos-Moreno Sergio, 177, 264
 Sau Salvatore, 278
 Schaefer Micha, 275
 Schmidt Dana Laureen, 245
 Schmidt Matthias, 22
 Schmidt Thomas, 45, 196
 Schmit Henri, 221

ENERSTOCK 2021

Sciacovelli Adriano, 71, 152
 Segarra Mercè, 167
 Sekavčnik Mihael, 173, 268
 Senegačnik Andrej, 173
 Serrano Ángel, 163, 177
 Sevault Alexis, 84, 134
 Shimizu Yuto, 212
 Shinoda Yasunari, 144
 Shockner Tomer, 107
 Shuster Michael, 39
 Silveira Elena, 264
 Smeacetto Federico, 9, 52
 Smiljanić Milutin, 47
 Solano J. Pedro, 189
 Sørensen Per Alex, 16, 45
 Sötz Veronika, 165, 185
 Spadoni Annarita, 278
 Spale Jan, 38, 112
 Srivastava Shreyas, 108
 Stahl Veronika, 81, 85, 219, 255
 Stamatiou Anastasia, 32, 57
 Stefanidou Maria, 281
 Steinbrecher Julian, 165, 185
 Stephan Andreas, 149
 Stoffel Phillip, 137
 Strehlow Andreas, 187, 194
 Stritih Uroš, 2, 46, 65, 80, 173, 182, 195, 207, 239, 251
 Stropnik Rok, 65, 173, 207, 251, 268
 Struhala Karel, 229
 Svobodova Adela, 161, 231, 248

Š

Šala Martin, 47

T

Tafelmeier Stefanie, 54, 233
 Takasu Hiroki, 86, 144
 Takeuchi Masakazu, 144
 Tan Chun Liang, 175
 Teigland Rune, 41
 Tezcan Fatih, 147
 Thess Andre, 241
 Thoen Jan, 283
 Thonon Maxime, 215
 Tizzoni Anna Chiara, 278
 Tombrink Jonas, 114
 Tomc Urban, 182
 Torbarina Fran, 82
 Torres-Rivas Alba, 113
 Tosatto Alice, 17, 176, 191, 196
 Toutain Jean, 90
 Traxler Ines, 472
 Trieb Franz, 241
 Trp Anica, 82
 Turchetti Luca, 278

U

Uden Jonathan, 211
 Uhlig Ulf, 127
 Ulldemolins Guillermo, 222
 Urban Adrià, 167
 Urbaneck Thorsten, 34, 117, 127, 198
 Urchueguía S. Javier, 39

V

Vallès Manel, 256
 Van Bael Johan, 203
 van Helden Wim, 7, 21
 Varvaggiannis Stratis, 187, 194
 Veca Elisabetta Maria, 278
 Venturi Elisa, 176
 Verbeeck Jef, 203
 Vérez David, 118, 138, 187, 193, 209
 Vetter Peter, 81, 85, 219, 255
 Vidal Karmele, 158
 Vidi Stephan, 149
 Villada Vargas Carolina, 60, 180
 Vullum-Bruer Fride, 134

W

Wagner Waldemar, 21
 Wallner Gernot, 8, 42
 Walter Heimo, 32
 Wang Diyue, 88
 Wang Gang, 139
 Wang Xiaolin, 280
 Weber Rebecca, 19
 Weiss Julius, 105
 Weller Thilo, 125
 Westermann David, 78
 Wood Colin, 280
 Wördemann Michael, 34
 Worlitschek Jörg, 32, 57, 238
 Wu Di, 109, 273

X

Xiao Shengqing, 34, 117
 Xu Tianhao, 69, 132, 139

Y

Yang Jiachuan, 151
 Yang Shufan, 280
 Yang Xinyan, 109, 273
 Yerlikaya Gurbet, 147
 Yoshida Saki, 86

Z

Zabukovec Logar Nataša, 23, 29, 80, 97

ENERSTOCK 2021

Zaki Abdelali, 158, 261
Zalewski Laurent, 215
Zauner Christoph, 242
Zavašnik Janez, 14
Zavrl Eva, 65, 182, 207, 251
Zelič Klemen, 271
Zettl Bernhard, 95
Zhang Shicong, 109, 273
Zhang Yimeng, 280

Zhao Changying, 136
Zhao Yanqi, 261
Zhao Yao, 136
Zhelezny Vitaly, 123
Zhu Jiang, 169
Ziskind Gennady, 107
Zorrilla David, 246
Zsembinszki Gabriel, 115, 126, 138, 187, 193, 209
Zunft Stefan, 241

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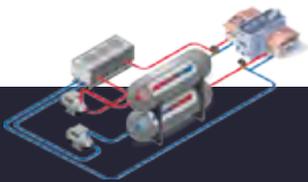
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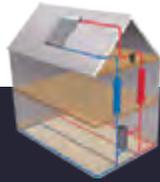
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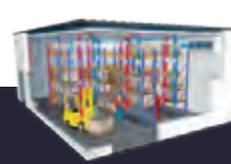
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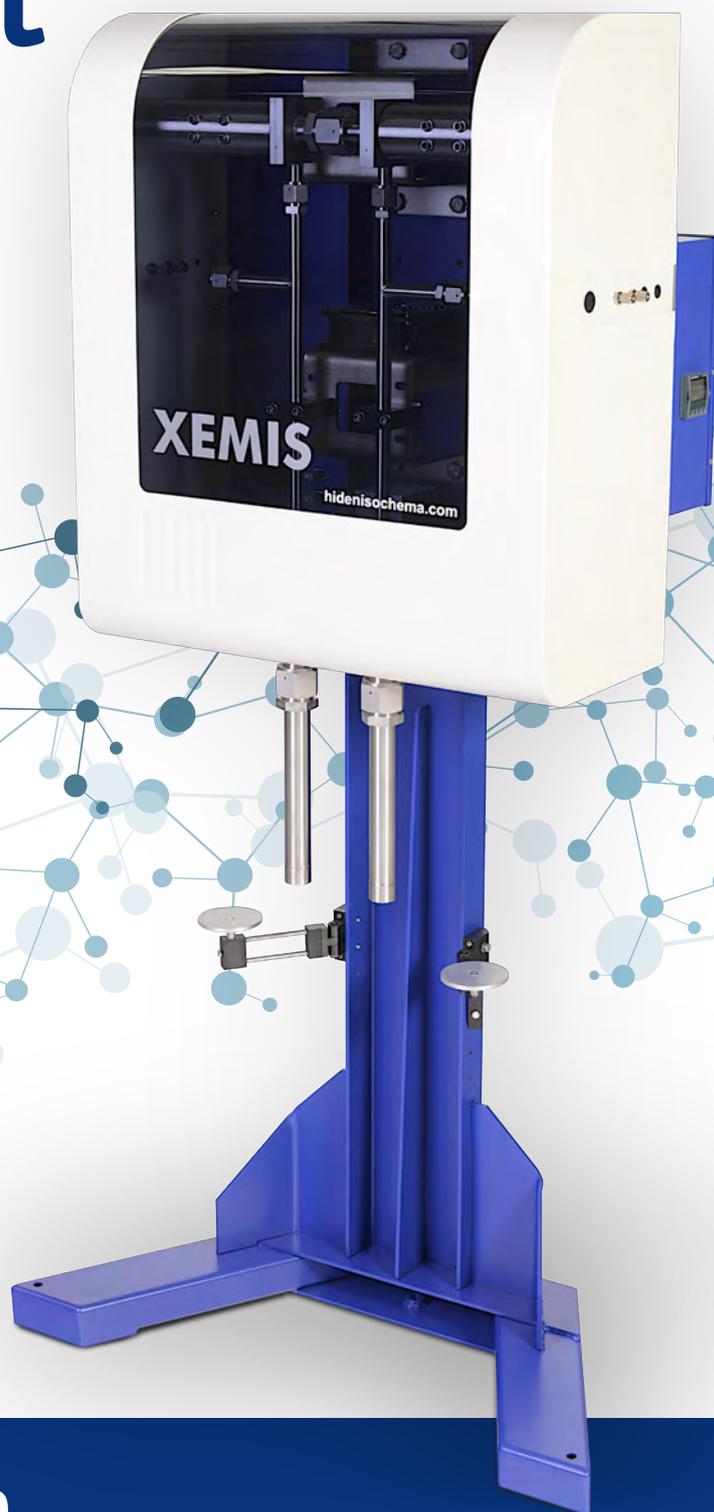
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SLOVENIAN LARGEST HEAT PUMP: THE “LUSTY” PROJECT

Slovenia's most famous vegetables producer, has been even more efficient since 2018; they are using a special heat pump - lower cost and higher efficiency.

Greenhouses need exactly the right conditions (appropriate heat and moisture) at the right time in the growth cycle to cultivate the tastiest vegetables, no matter what the weather's like outside. To get best vegetables greenhouses sometimes even need heating during the summer months.



The greenhouse is spread on almost 1,2 km²

Choosing the right heating system is vital for this kind of production, so growers can produce delicious taste at minimal cost.

That's how Kronoterm started developing the biggest heat pump in Slovenia in 2017; its heating capacity is 2000 kW, and it was installed and commissioned in 2018.

Until 2018, investor's greenhouses had been heated only by geothermal water from a geothermal borehole, with additional heating provided by natural gas. Rising heating costs due to an expanding greenhouse and environmental demands meant the existing conditions no longer meet their increasing needs for thermal energy.

By installing a new Kronoterm heat pump, they wanted to streamline their use of geothermal energy, while reducing costs and their environmental impact at the same time. They succeeded in gaining from 2 MV of additional heat and lowering the need for natural gas, which comes at a high cost.

Savings of up to 72% compared to natural gas and producing up to 50 % less CO₂ emissions

Kronoterm's new and unique heat pump for the investor's greenhouse turns out a remarkable 2 MW. This is enough power to heat a community of 400 low-energy houses at an average size of 140 m² (an average new building). The working efficiency of the COP heat pump is also excellent, varying between 5.1 and 6.0. This means 1 unit of electrical energy input to power the heat pump yields as many as 5 to 6 units of heat energy, far exceeding the expectations of both the heat pump's developers of as well as its investor. The entire investment was recovered in less than a year (ROI < 1 year) due to the negligible heating costs. The investor is thrilled to say that the new system is as much as 100 % efficient in pumping geothermal energy from an incredible depth of 1500 m.

“I can proudly say that we developed the biggest geothermal ‘heat recovery’ heat pump system in Slovenia and the wider region. The technology at work is also a bit different – it uses waste geothermal heat from the borehole with a relatively high temperature – between 30 and 40 degrees Celsius. The end temperature is also relatively high, as it reaches between

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65 and 80 degrees. Results show that the geothermal energy efficiency after installing the heat pump is almost one hundred per cent.” said director Bogdan Kronovšek.

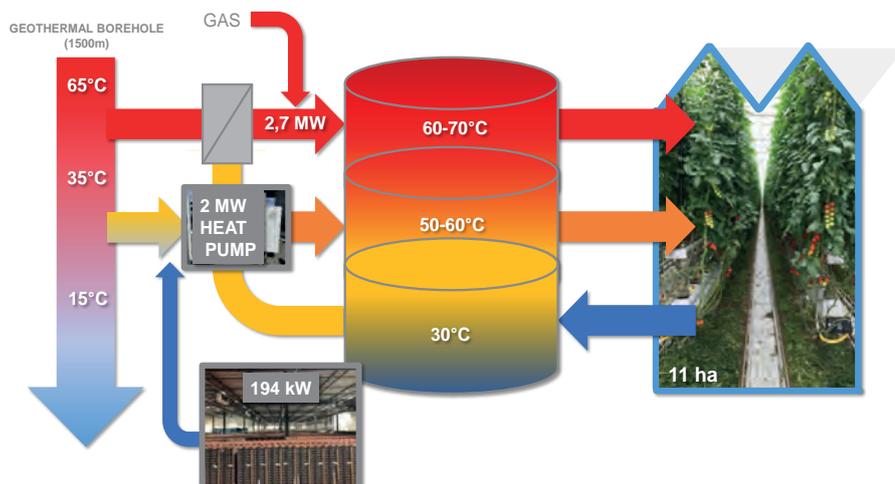
They managed to cool the water temperature from 65 to 10-15 degrees (depending on the flow control). The savings in comparison with the prior use of natural gas are as high as 72 per cent and our CO₂ emissions have decreased by about 50 per cent. The heat pumps are expected to produce around ten thousand megawatt hours per year, which was exceeded by approximately 20 % in the first year alone.

The Kronoterm heat pump doubles savings because it both heats the greenhouse and cool vegetables in warehouse.

The name ‘heat pump’ alone tells us what the device does – it pumps heat from a lower energy heat source like geothermal water into a higher energy heat system such as a greenhouse. Such a machine can also pump heat from other sources, like the air. This is exactly why Kronoterm upgraded investor heat pump with a special system that also lets them pump heat from the vegetables warehouse, which it then cools to the optimal storage temperature. This revolution in the Kronoterm system was a double success. First, they lowered their investment costs because the investor had no need to install an additional cooling device of at least 200 kW. Second, waste heat drawn from storage is reused for greenhouse heating. If an independent cooling device were installed, this energy would be wasted.

The special heat pump was designed, developed and built entirely by Kronoterm, from development to execution. Kronoterm uses knowledge and commitment to reinvent what is possible in using heat pump technology in ways that ensure satisfied partners, users, and even the environment.

For more info visit www.kronoterm.com, or contact them at info@kronoterm.com.



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