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WG A1: Engineering and processing of PCMs, TCMs and sorption materials

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Abstract

An overview on the recent results on the engineering and characterization of sorption materials, PCMs and TCMs investigated in the working group WG A1 “Engineering and processing of TES materials” of IEA SHC Task 42 / ECES Annex 29 (Task 4229) entitled “Compact Thermal Energy Storage” is presented.

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1. Introduction

Thermal energy storage is an important technology for renewable energy systems and energy efficiency and is essential particularly for solar thermal systems. It is necessary to store heat efficiently for longer periods of time. Until now, no cost-effective compact storage technologies are available to do this. It is well known that materials are one of the main challenges for finding effective solutions for thermal energy storage, and that there is a need for new storage materials with a higher specific energy storage density and lower material cost.

One of the scopes of Working Group A1 “Engineering and processing of TES materials” is the engineering of thermal energy storage materials by changing the properties of existing materials and developing new materials with better performance, lower cost, and improved stability. The materials under consideration are those relevant to thermal energy storage using phase change, chemical reactions as well as sorption technologies. The activities of the working group include the synthesis of new materials, determination of material characteristics, determination of the material structure and composition, which influence the material performance, and determination of the role and importance of material containers.

The second aim of this working group is the processing of the raw materials, such as finding optimal methods for micro- and macro-encapsulation of storage materials (particularly phase change and thermochemical materials), processing of phase-change slurries and finding new combinations of materials (composites).

In the framework of the IEA SHC Task 42 / ECES Annex 29 (Task 42-29), significant R&D effort was directed toward the development of new or improved TES materials. Here, some contributions of several research groups, which are actively involved in this working group, are shown.

2. TES materials

2.1. Phase change materials

Phase change materials (PCMs) used for thermal energy storage are an important class of materials which substantially contribute to the efficient use and conservation of waste heat and solar energy. The storage of latent heat provides a greater density of energy storage with a smaller temperature difference between storing and releasing heat than the sensible heat storage method. Many different groups of materials have been investigated during the technical evolution of PCMs [1, 2].

Main issues covered PCMs during period (2013-2015) of the IEA SHC Task 42 / ECES Annex 29 (Task 42-29) are: i) PCMs for seasonal storage applications, including inorganic and new organic mixtures undergoing severe and stable undercooling; ii) low-cost PCMs coming from waste, by-products or natural resources; iii) solid-solid PCMs with enhanced stability; iv) micro/nano-encapsulated organic PCMs and microcomposites with improved performances; v) sugar-alcohol based PCMs for application at low-to-medium temperatures; vi) new PCM emulsions for cooling and industrial applications and vii) corrosion of metal and polymer containers in contact with different commonly used PCMs. Significant effort has also been done regarding the integration of PCMs into the applications, such as works related with façades and construction materials including PCMs or PCMs macro-encapsulation. New eutectic mixtures of organic or inorganic PCMs for applications at low temperature have also been produced and tested. Furthermore new imaging techniques based on infrared thermography were developed for PCMs to determine phase diagrams in record time, heterogeneous nucleation rates on flat substrates as well as temperature-dependent crystal growth rates with measurement of the temperature rise at the solid-liquid interface.

The recently finished COMTES research project (European FP7-energy program) evaluated the use of sodium acetate trihydrate (Technical University of Denmark and Graz University of Technology Austria). This salt hydrate was identified as potential PCMs for super cooling PCM heat storage, because of its large melting enthalpy (between 226 and 264 kJ/kg) and its price of 2.5-3 €/kg. Material's properties like solubility, density, thermal conductivity, heat content and dynamic viscosity were determined.

Researchers at University of Zaragoza, Spain, developed a characterization methodology for low cost PCM materials as cost is one of the most important aspects to enable their commercial expansion. This methodology has been applied to 37 samples. The complete characterization encompassed measurements of specific heat, thermal diffusivity, density, thermal conductivity, enthalpy and viscosity, as well as its resistance to thermal cycles. In this

manner it can be possible to select the material and to design correctly the system for its use. The results showed: 9 high potential, 4 potential, 21 low potential and 4 null potential storage materials. The high potential storage materials included 4 paraffin materials with phase change around 50°C-70°C and latent heat of fusion (H_f) around 250 J/g, 2 natural products with phase change between -10°C and ambient temperature and H_f around 200 J/g, 2 fibres by-products with phase change below zero and H_f around 200 J/g and one polymer with phase change around 60°C and H_f around 200 J/g and one with phase change between 90°C and 180°C and H_f around 300 J/g. All samples showed stable properties after thermal cycling (25 cycles) [3].

At University of Artois in France the study of the thermo-physical characterization of a composite of cement mortar integrated with 20% of micro-encapsulated PCM was carried out within an original set-up [4]. This study showed that the energy stored or released was 41% higher than the energy stored (released) by the conventional mortar in the temperature range to be observed in solar wall. The advantage of this material was that super cooling effect was not present and that the difference in thermal behaviour between fusion and cooling processes remained observable.

A new type of ventilated active façade that includes phase change materials (PCMs) in its outer layer was developed and tested at University of the Basque Country, Spain. A real-scale sample of 2.7m x 2.7m was constructed and evaluated through a PASLINK test cell [5, 6]. The façade was composed of five different layers, while the external sheet included 50 kg of RT35 from Rubitherm GmbH as PCM. This external layer was formed by an aluminium macroencapsulation system, comprised by hollow aluminium rectangular profiles placed horizontally which contained the PCM inside. Experimental results of the façade showed that the melting-solidification processes that took place in the PCM led to an increase in the heat absorption during the phase-change temperature intervals, which reduced overheating of the façade. Because of the PCM solidification, 2.5 hours after the solar radiation faded out, the air circulating through the chamber was still warmed by 2 °C. A finned flat plate latent heat thermal energy storage system for domestic hot water applications was developed by Campos-Celador et al [7]. The system could be applied to micro-cogeneration systems or solar thermal devices. It was basically formed by rectangular macroencapsulation plates arranged in series and parallel forming stacks. Water was used as a heat transfer fluid and the material employed to build the plates was aluminium. The PCM used was RT60 from Rubitherm GmbH and it was placed within the finned flat plates. An experimental prototype was constructed and tested in a suitable pilot plant. Three new binary mixtures of sugar alcohols comprising erythritol, sorbitol and xylitol for thermal storage applications in the heating and domestic hot water temperature ranges were studied [8]. Eutectic compositions underwent melting temperatures of 83.9, 86.6 and 74.9 °C, for the erythritol–xylitol; erythritol–sorbitol and xylitol–sorbitol systems, respectively. Regarding the heat storage ability, the erythritol–xylitol eutectic composition showed the largest melting enthalpy of 248.7 J/g. Experimental measurements performed by polarized thermomicroscopy showed that the mixtures presented a low crystallization rate, which limits their use in short term LHTES (Latent Heat Thermal Energy Storage) systems.

At University of Gaziosmanpaşa, Turkey, several micro/nanoencapsulated PCM materials were synthesized and characterized. Micro/nanoencapsulated capric, lauric and myristic acids (PCMs) with polystyrene (shell material) melted and frozen in the temperature range of 22-48°C and 19-49°C as they stored and released latent heat in a range of 87-98 J/g and (-84) J/g-(-96) J/g and they had good thermal durability and reasonable thermal conductivity values [9]. These advantageous properties make them potential LHTES materials for thermal regulating, solar heat pumps and solar space heating-cooling applications in buildings. Polymethylmethacrylate (PMMA)/capric-stearic eutectic mixture (C-SEM) micro/nano capsules were synthesized effectively using emulsion polymerization method. PMMA/C-SEM (1:2) micro/nano capsules showed a melting temperature of 21.37°C, which can be suitable for free cooling of buildings depending on the climatic conditions. It had a latent heat of melting of 116.25 J/g, which can be enough to integrate with conventional building materials [10]. Polystyrene (PS)/n-heptadecane micro/nano-capsules as a novel encapsulated phase change material (EPCM) were prepared. The melting temperature and latent heat of the prepared EPCM were measured as 21.48°C and 136.89 J/g, respectively. The material had good thermal durability. Thermal reliability, chemical stability, thermal conductivity and phase change reversibility of the micro/nano-EPCM were also studied. All of the results revealed that the fabricated PS/n-heptadecane micro/nano-capsules had promising LHTES potential especially for passive solar thermal regulation of textile, building, food storage container, medical and electronic materials [11]. Micro/nano encapsulated paraffin eutectic mixtures (PEMs) with polymethylmethacrylate (PMMA) shell were prepared by emulsion polymerization. The micro/nano capsules

containing the highest PEM content had melting temperature range of about 20–36°C and latent heat storage capacities of about 86–169 J/g. Thermogravimetry analysis results verified that the encapsulated PEMs had good thermal reliability and chemical stability after repeated melting/freezing cycles for 5000 times.

At KTH-Royal Institute of Technology, Sweden, erythritol, xylitol and PEG 10,000 were investigated preliminarily with Temperature-History (T-history) method. This was on a study on polyols as phase change materials (PCM) for low-temperature surplus TES. For erythritol and xylitol some thermally activated change after three to five heating/cooling cycles, and for xylitol some glass transition was evidenced. For erythritol, two different melting temperatures, 118.5–120°C and 106–108°C at different cycles and an average subcooling of 18.5°C were observed. The average fusion enthalpies of the materials tested are found to be: 169 kJ/kg (PEG 10,000), 284 kJ/kg (erythritol) and 159 kJ/kg (xylitol) [12].

The influences of particle size and surface molecules on nucleation temperature/subcooling of n-octadecane/water emulsion and microencapsulated n-octadecane have been investigated at ISE Freiburg, Germany. A series of PMMA-encapsulated paraffin with various particle sizes (0.5 to 1000 µm) have been synthesized. Differential scanning calorimeter analysis showed that subcooling increases with decreasing particle sizes. Furthermore DSC analyses of emulsions with different non-ionic surfactants (e.g. Tween/Span 60/80 and PVA) have been compared. The results indicate that surfactants with paraffin-like lipophilic parts could reduce subcooling. In the German project KOLAN (03ESP357B) PCM emulsions were developed for cooling of buildings and for technical and industrial applications. The influence of non-ionic emulsifiers on the stability, viscosity and thermal behaviour of paraffin/water emulsions was examined. Therefore octadecane concentration has been kept at 30 wt. % whereas the emulsifier concentration and mixtures of emulsifiers varied. This emulsion provided storage capacity of 90 kJ/l. Stability was measured in a remoter while applying thermal and mechanical stress by shearing the emulsion at a defined heating rate. The viscosity showed always values below 20 mP as which is important to keep the pumping energy consumption low.

At ZAE Bayern, Germany, new organic PCM mixtures were developed and characterized with DSC and T-History methods. Binary mixtures of linear alkanes with saturated fatty acids (group I) and linear alkanes with monohydrated alcohols (group II) were found to form eutectic systems: hexadecane + caprylic acid (35:65), nonadecane + capric acid (40:60), pentadecane + undecanol (55:45), icosane + myristil alcohol (30:70). Measured enthalpy curves of the mixtures were comparable with the basic materials in terms of enthalpy change, phase change width and degree of subcooling. Thus, an adjustment of melting temperatures without losses in terms of melting enthalpy was obtained by mixing organic PCM of different material groups [13]. Furthermore a three-step method to determine the eutectic composition of a binary or ternary mixture was developed [14]. The method consists of creating a temperature–composition diagram, validating the predicted eutectic composition via differential scanning calorimetry and subsequent T-History measurements. The method was tested with two binary mixtures: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$. To determine the maximum storage capacity of the two eutectic mixtures, a temperature range of 15 K was chosen around the phase transition for both eutectic mixtures, i.e. a temperature range from 5 to 20°C and 5 to 10°C for $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$, respectively. An enthalpy change of about $172 \text{ J} \cdot \text{g}^{-1}$ ($302 \text{ J} \cdot \text{cm}^{-3}$) and $162 \text{ J} \cdot \text{g}^{-1}$ ($274 \text{ J} \cdot \text{cm}^{-3}$) was determined from the DSC heating curves for $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$ and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3$, respectively.

The study on chitosan-gelatine (CG) microcapsules containing either caprylic (melting point; 15–17°C) or decanoic acid (melting point; 29–33°C) was performed at Nigde University, Turkey, and Cukurova University, Turkey. Microcapsules/microcomposites were prepared via complex coacervation and cross-linked by glutaraldehyde. They achieved to develop caprylic acid/CG microcapsules with a mean diameter of 0.22 µm and decanoic acid/CG microcomposites with a mean diameter of 1.06 µm via complex coacervation. FTIR (Fourier Transformed Infrared Spectroscopy) results confirmed that the both caprylic and decanoic acid retained their chemical structure after microencapsulation with CG shells. The prepared microcapsules showed microcapsules synthesized successfully with a melting temperature close to 11.5°C and a latent heat storage capacity of approximately 79 J/g. Given the non-toxic, biocompatible, and biodegradable properties of gelatine and chitosan, as well as the thermal properties of the resultant products, these capsules can be used in food package applications to ensure temperature-controlled packaging and transport [15].

Corrosion effects of metal and polymer containers for use in PCM energy and cold storage, cooling and heating applications were studied at University of Barcelona and University of Lleida in Spain. PCM are usually encapsulated in containers, hence the compatibility of the container material with the PCM has to be considered in order to design a resistant container. Four different PCMs (SP21E, PureTemp23, Ca/Pa eutectic, Ca/My eutectic) were put in containers of different metals/alloys (aluminium, copper, carbon steel, stainless steel 304 and stainless steel 316) and tested. Results showed corrosion on aluminium specimens hence caution must be taken when selecting it as an inorganic salt container. Despite copper had a corrosion rate range of 6–10 mg/cm²/yr in the two tested fatty acid formulations it could be used as the container. Stainless steel 316 and stainless steel 304 showed great corrosion resistance (0–1 mg/cm²/yr) and its use would totally be recommended with any of the studied PCM [16]. Eleven salt hydrate PCMs (S10 and S46 by PCM Product, C10 and C48 by Climator, ZnCl₂·3H₂O, NaOH·1.5H₂O, K₂HPO₄·6H₂O, MgSO₄·7H₂O, Zn(NO₃)₂·4H₂O, K₃PO₄·7H₂O and Na₂S₂O₃·5H₂O) were placed in copper, aluminium, stainless steel 316 and carbon steel containers and evaluated for heating and cooling applications. Tests for cooling applications showed that commercial S10 was recommended for the use with stainless steel and aluminium, but the latter only according to the specific application. On the other hand, commercial PCM - C10 was suitable to be encapsulated with both aluminium and stainless steel. PCMs used for cooling applications (NaOH·1.5H₂O, ZnCl₂·3H₂O and K₂HPO₄·6H₂O) showed low corrosion rate when they were in contact with stainless steel. NaOH·1.5H₂O was also suitable for working with carbon steel depending on the application while ZnCl₂·3H₂O and K₂HPO₄·6H₂O could work also with copper, depending on the application. Regarding heating applications, all tested PCMs presented very low corrosion rate when working with stainless steel. Commercial S46 was also recommended for the use with aluminium according to the application. The other commercial PCM (C48) showed low corrosion rate with carbon steel and aluminium as well. Besides, MgSO₄·7H₂O was recommended to be used with aluminium, K₃PO₄·7H₂O presented low corrosion rate with carbon steel and Na₂S₂O₃·5H₂O can also be used with carbon steel and aluminium [17]. Four common metals as PCM containers: copper, aluminium, stainless steel 316, and carbon steel and four polymer materials as PCM containers were selected: polypropylene (PP), high density polyethylene (HDPE), polyethylene terephthalate (PET), and polystyrene (PS) to study the corrosion effect of different metals and polymer materials in contact with some PCM used in low temperature applications. Nine PCM formulations were analysed: three of them were based on commercial options ClimSel-18 (C-18) from the company Climator, E-21, produced by Cristopia, and E-21 with 1% of oxyethylmethyl cellulose (CMC) to thickening the solution. The rest of them were their own formulations [18]: PCM-D:19% NH₄Cl + H₂O, PCM-E: PCM-D + 1% CMC, PCM-F: PCM-D + 3% AlF₃, PCM-G: PCM-F + 1% CMC, PCM-H: PCM-D + 3% NaCl, PCM-I: PCM-H +1% CMC. Results showed that copper and carbon steel must be avoided as PCM containers, and aluminium was not recommended as well; while stainless steel 316 was recommended. Moreover, PP, PS, PET, and HDPE were not affected by a process of degradation and were also compatible with these PCMs. Thermal stability of sugar alcohols as phase change materials for medium temperature energy storage application was tested. Three promising sugar-alcohols were selected: D-mannitol, myo-inositol and dulcitol under high melting enthalpy and temperature criterion. D-mannitol and dulcitol presented poor thermal stability. Myo-inositol showed almost no decrease in thermal properties after 50 cycles for the heating process, however in the solidification part a decrease of 20% of enthalpy and 11% of temperature values was observed [19]. D-mannitol was selected for testing it in a solar cooling application due to its melting point (167°C) and a relatively high enthalpy (316.0 kJ/kg). The experiments performed by DSC have shown that the d-mannitol presents polymorphic structural changes and, therefore, its thermal properties are not always the same. Depending on the polymorphic phase obtained, d-mannitol has different melting temperature. This behaviour was corroborated in a storage tank, where it may be seen that the cooling rate of the d-mannitol is a key parameter in the formation of the different polymorphic phases [20, 21]. D-mannitol and hydroquinone were used at real solar cooling plant. For the same boundary conditions, the energy stored by d-mannitol was higher than that for hydroquinone [22].

At I2M, University of Bordeaux, France, the enhancement of latent heat by confinement of the PCM in a nanoporous structure or by addition of nano-fillers within the PCM or both was studied. Thus multi-walled carbon nanotubes (MWCNTs) were dispersed in paraffin wax RT65 obtained from Rubitherm Technologies GbmH (T_m ~ 64°C) by melt blending method. Composites with MWCNTs loadings of 0, 0.25, 0.50 and 1 wt.% have been prepared. DSC tests showed that the addition of MWCNTs did not lead to significant changes in the melting range of temperatures, although the onset temperature was slightly increased. However, the expected diminished value of

the latent heat due to the replacement of the paraffin by fillers was not observed at all. On the contrary, the latent heat was significantly and progressively raised when the mass fraction of MWCNTs increased [23]. In the recent European project SAM.SSA (Sugar Alcohols based Materials for Seasonal Storage Applications, FP7 2012-2015) new sugar alcohol (SA) based materials for solar thermal seasonal storage applications have been developed and studied in-depth [24, 25]. SAM.SSA developments include new SA-based eutectic mixtures lowering the original high temperatures of the single materials, low-cost tailor-made carbon porous structures and corresponding carbon/SA composites with enhanced thermal conductivity, and SA micro-encapsulation. A new solution for efficient SA crystallization was also established. In general, SA with high heats of fusion often exhibited high melting temperatures ($>100^{\circ}\text{C}$), which limited the choice of heat transfer fluids to be used. This was particularly discussed in solar heating and DHW applications, where cheap water-based solar collectors were required. It was established that new true eutectic mixtures using SA could be manufactured lowering the original high temperatures of the single materials. These new mixtures were proven to have relatively high latent heat (245-300 J/g), proper melting points ($77\text{-}87^{\circ}\text{C}$), and an evident subcooling effect which enabled low-cost long-term storage schemes. The studied materials were also characterized by high density values (1.3-1.4 g/cc in liquid) and moderate-to-low volume changes ($<10\%$). Achieved energy density by melting under usual working condition was comparable (even higher) to that of sorption-base storage technologies. The values ranged between 120-190 kWh/m³. Thermal conductivity values in solid state ranged from 0.8 to 1.4 W/m/K for the SAs, and from 0.2 to 0.4 W/m/K for the SA-blends. In liquid, all the studied materials showed thermal conductivity values around 0.35-0.45 W/m/K. The specific heat was 1.4 to 2 times lower than that of water. In summary, SA and SA-mixtures performed better than most of organic PCMs and showed performances similar to that of salt hydrates. However, SAs are not concerned by segregation, separation or corrosion issues which are the major drawbacks of salts hydrates. In-depth understanding of nucleation and crystal growth processes had been achieved. It was proven that the low nucleation rates which characterized sugar alcohols were due both, to the low atoms mobility imposed by highly viscous undercooled liquids and to the molecular conformational changes accompanying the liquid-to-solid transitions. Temperature dependent crystal growth rates were experimentally determined and indicated that all studied materials showed diffusion-limited crystal growth kinetics. As expected, the materials with stronger undercooling were those with lower crystal growth rates. The maximum growth rates of D-mannitol and erythritol were, respectively, 1000 $\mu\text{m/s}$ (at 127°C) and 520 $\mu\text{m/s}$ (at 57°C). They were about two orders of magnitude lower for adonitol (13 $\mu\text{m/s}$ at 77°C), L-arbitol (2.5 $\mu\text{m/s}$ at 73°C) and xylitol (3 $\mu\text{m/s}$ at 67°C). The maximum value of the growth velocity was lower than 1.5 $\mu\text{m/s}$ for all SA-blends. Overall understanding of the bubbling-crystallization process was provided and key related variables and parameters were identified. Commonly used crystallization techniques, including cooling, intentional seeding, ultrasonication and antisolvent-crystallization, were studied at first but proved to be inefficient. On the contrary, air bubbling was a simple solution which seemed to be effective and robust in triggering the SA nucleation and in accelerating total crystallization rates. The proof of the concept was achieved at the laboratory scale using small reactors (300-900 ml). It was also shown that combining solvent-antisolvent systems with bubbling can have very positive effect on SA crystallization. Furthermore new imaging techniques based on infrared thermography were developed for PCMs to determine phase diagrams in record time, heterogeneous nucleation rates on flat substrates as well as temperature-dependent crystal growth rates with measurement of the temperature rise at the solid-liquid interface at this institute. First method establishes a preliminary phase diagram in a very short time (<3 h) that can then be refined by more detailed but more time consuming techniques. The interest has been to speed the "screening" steep which often precedes the development of a new material, in which a large number of systems and/or mixtures have to be tested [26]. The second method allows studying heterogeneous nucleation on flat substrates in a quantitative way. This method is based on the experimental observation, by using an infrared camera, of the cooling process of a large number of sub-millimetre droplets deposited on the substrate to be studied. When a droplet crystallizes, a peak is observed in the corresponding infrared signals. This peak reflects the sudden heating of the droplet due to the release of latent heat of crystallization. It allows to identify the temperature at which each droplet crystallizes and, therefore, to calculate the probability of nucleation or, alternatively, the nucleation rate as a function of the supercooling [27]. In the third method [28], the optical microscope (or CCD camera) is replaced by an infrared camera which, after calibration, allows measuring the temperature at any point of the solid-liquid interface at any time. The interest of the method has been highlighted by studying the crystal growth kinetics of sugar alcohols.

2.2. Thermochemical materials

2.2.1. Salt hydrates

Thermochemical energy storage has the potential to store heat energy ten times more than sensible and three times more than latent heat storage technologies. This technology includes chemical storage and sorption storage. Chemical storage consists of producing a reversible chemical reaction. In heat utilization processes, the dehydration (forward reaction) is used for charging, and the hydration (backward reaction) of the material for discharging the heat from the storage unit. The performance of the system during discharging is realized by exothermic reaction and the performance during charging is realized by endothermic decomposition reaction. Salt hydrates were selected because their high energy density and low cost make them advantageous, their main disadvantages being their lower stability and relatively slow kinetics. In order to overcome these disadvantages some studies have been performed.

At Leuphana University, Germany, a study on 45 salt hydrates regarding their nontoxicity, high energy density and low cost has been conducted for low temperature thermochemical heat storage application, and only 17 of them showed reversible reaction. Further investigations showed, that only three salt hydrates were usable depending on a reactor simulation in their project “Thermal Battery” for private households and industry applications: $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ (392 kWh/m³), $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (359 kWh/m³) and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ (340 kWh/m³). The hydrates of calcium chloride (353 kWh/m³) challenged the use as storage material and it was a representative for other potential storage materials (e. g. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (351 kWh/m³)) [29]. Therefore, the economic and the physical properties were reflected as well as the use in applications of adsorption cooling and heating, absorption processes, desiccation, dehumidification and thermal storage were reviewed. Besides advantageous characteristics like storage energy density and nontoxic properties the formation of solution during hydration of the pure salt hydrates decreased the cycle stability and disabled their use as the storage material. One possibility to avoid this disadvantage was the control of temperature and water vapour pressure. If the supply of water vapour flow was limited it was possible to avoid the formation of solution ($\text{MgCl}_2 \cdot 4.5 \text{H}_2\text{O}$) [30]. However, this procedure was not manageable in macro scale because of the heterogeneous reactions occurring in the storage bulk. On the other hand mixing calcium chloride with magnesium chloride preserved cycle stability. Surprisingly the experiments showed that the cycle stability did not change despite the presence of over-hydration. Also the impregnation of salt hydrates into porous carbon materials and vermiculite prevented deliquescence and improved the diffusion of water vapor into the material, the cycle stability and heat conductivity [31, 32], but decreased the energy density. Heat exchanger modelling and lab scale experiments were done with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ [33]. It revealed that even normal solar panel can activate charging at 90 °C, though the complete charging would be finished at 120 °C.

Corrosion tests between inorganic TCM and metal vessels together with thermal cycling stability have been performed at University of Barcelona and University of Lleida in Spain. This study presented the results of an immersion corrosion test following ASTM G1 simulating an open TCM reactor, under humidity and temperature with defined conditions. Four common metals: copper, aluminium, stainless steel 316, and carbon steel, and five TCMs: CaCl_2 , Na_2S , CaO , MgSO_4 , and MgCl_2 , were studied. Copper can only be recommended with caution when combined with CaCl_2 and MgCl_2 . This metal has been mostly used as heat exchanger material because of its high thermal conductivity. Therefore, a coating is needed to protect the metal corrosion from the TCM. Carbon steel is slightly corroded with CaCl_2 and Na_2S , forming a brittle corrosion layer on the surface. Aluminium and copper showed severe corrosion when combined with Na_2S , aluminium corrosion was more significant since the specimen was totally destroyed after 3 weeks. Only stainless steel 316 can be recommended for the use as a metal container material for storing all these tested TCMs [34]. Thermo-physical characterization and thermal cycling stability of two TCMs: CaCl_2 and zeolite were examined. In this study the performance of CaCl_2 following a chemical reaction and zeolite (a sorption process) was compared for seasonal/long term storage. The main results showed that the chemical TCM was more energy-efficient than the sorption TCM. The CaCl_2 calculated energy density was 1.47 GJ/m³, being the best option to be considered to be used as TCM, even though the dehydration process of the zeolite was simpler and it happened at higher temperatures its calculated energy density was only 0.2 GJ/m³ [35].

2.2.2. Sorption materials

A specific type of TCM is sorption storage. Sorption materials attract broad interest because of their potential applicability in the field of thermal energy storage, e.g. low temperature sorption heat storage, which is based on a reversible physico-chemical process: adsorption/desorption of water on porous solid sorbents. Solid/vapor adsorptive systems are very promising for heat transformation applications as they can utilize efficiently solar energy or waste heat as driving force.

At Technical University of Applied Sciences Wildau, Germany, achievements in material development and characterization for seasonal compact thermal adsorption storage within the frame of COMTES have been performed. The proposed material for the compact thermal adsorption storage consisted of binderless beads of zeolite X with a large micropore volume. This molecular sieve with chemical composition $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : m\text{SiO}_2 : n\text{H}_2\text{O}$ with $m \leq 2.35$ showed high water adsorption capacity and high thermal storage capacity. Furthermore, zeolites with a lower Si/Al-ratio but the same structure (NaYBF) have been taken into account. Both are product of the Chemiewerke Bad Köstritz (CWK) in Germany. Both zeolites had the advantage to be binder-free, meaning that they showed about 15% higher water adsorption capacities compared to adsorbents with binder. From detailed material characterization it has been found that both zeolites showed similar water adsorption capacity of slightly above 30 wt.%. However, 13XBF revealed higher adsorption heat and better kinetics compared to NaYBF (the difference between the zeolites was around 20-10 kJ/mol). For application in a seasonal heat store the high thermal energy output of the zeolite 13XBF seemed to be favorable, but higher temperature had to be provided from a solar thermal collector field for the water desorption process. From hydrothermal stability measurements it has been obtained that both types of zeolites showed no noteworthy degradation of their water adsorption capacity for the conditions expected in the seasonal sorption store (180 to 200°C, water vapor pressures in the mbar-range). They also tailored zeolite Y's adsorption properties by silicon enrichments for heat pump applications with low temperature heat as driving energy. By a partial dealumination of the parent zeolite Y by steaming the hydrophilic character of this zeolite was decreased which led to a lower desorption temperature for water. The reduction of the hydrophilic character of the conventional zeolite Y shifted the adsorption isotherms towards higher relative water vapor pressure and hence into the working area of adsorption heat pumps for low temperature utilization ($T < 100^\circ\text{C}$) [36].

Researchers at ISE Freiburg, Germany, improved sorption properties of activated carbon for specific application environments, such as the adsorption of water in an open sorption heat storage system. The optimization criteria have included all of the important parameters, such as production costs and the expense for primary energy, uptake or storage capacity, discharging power, and material stability during the typical service life of the product. The combination of a cost-effective source material and adapted modifications prepared sorption material that can compete in terms of sorption characteristics with materials that are significantly more expensive to produce. Particularly for adsorption-based thermal energy storage applications, this has been an important step towards economic and primary energy amortization of capital expenditures for thermal energy storage systems. 26 commercially available carbon materials as powder and granules were evaluated regarding the suitability of modification and water adsorption. 12 of them showed the best results. It was found out that these materials possessed pores in the range from 0.6 to 1.2 nm. Oxidation treatment was used for the modification of these AC materials. One of the first modified samples almost reaches the project-internal benchmark of water uptake of 0.3 g/g at relative pressure of 0.4.

Carbon was also used as a high thermal-conductive component in the preparation of the composite combining with microporous aluminophosphate (C-APO), which is the most promising water adsorbent in terms of equilibrium data, in order to enhance its thermal conductivity, at National Institute of Chemistry, Slovenia. Namely, this microporous aluminophosphate shows maximal water loadings of up to 32wt%, under relatively mild conditions, e.g. adsorption at 35°C (1,23kPa) and desorption at 95°C (5,67kPa). The advantages of this material are also the energy density in the working temperature range from 40 to 140°C of 240 kWh/m³, its hydrothermal and thermal stability (up to 900°C) and water desorption at 95°C. The main disadvantage of this material is its low thermal conductivity (~ 0.11 W/m/K) that reduces heat exchanges rates during sorption process. One of the strategies to improve thermal conductivity of the adsorbent is a combining aluminophosphate sorption material with material with high thermal conductivity, like porous carbon, in the form of coatings. The main condition for the preparation of

carbon coatings on aluminophosphate sorption materials is thermal and structural stability of sorption materials up to 700°C, because carbon coatings are usually prepared by high-temperature treatment (500-700°C) of carbon-containing organic materials (precursors) under inert gas in the furnace. This method is mainly used for the preparation of catalysts supports and electrode materials in superconductors and fuel cells. As carbon precursors, sucrose and citric acid have been used. The aluminophosphate sorption material was coated with a thin layer of carbon by wet impregnation and dry procedure, followed by carbonization at 650°C under inert atmosphere in the furnace. The results of structure analysis showed that the preparation methods of C-APO materials had great influence on the preservation of structure and its structural properties. It was found out that wet impregnation using solutions of citric acid caused destruction of the structure, while wet impregnation with sucrose solution did not affect the structure. The amount of carbon in the samples was dependent on the type of the used carbon precursors and on the method of the preparation and it was determined to be from 1.1 to 2.4 %. Water sorption capacity was obtained at different temperatures by gravimetric method and showed that composites had similar water uptakes, while determined heats of adsorption were lower for composite materials, which could be assigned to the presence of different amounts of carbon in the samples. The results of thermal conductivity measurements showed small increase of thermal conductivity of C-APO materials. Another strategy for the improvement of thermal conductivity was used by the preparation of aluminophosphate coating on metal plate. Water solution of aluminophosphate adsorbent and polyvinyl alcohol was deposited on cleaned stainless steel plate of 5 x 5 cm and dried overnight. The thickness of the coating was determined to be from 100 to 180 µm. The coated plate was tested of water sorption capacity and hydrothermal stability (4600 cycles). The APO coating showed similar shape of water adsorption curve as the powder material, with a steep rising of the uptake between 0.1 and 0.2 relative pressures, which is ideal for adsorption heat pumps. The mass specific uptake is lowered to some extent, due to the binder content in the coating. However there is no negative influence of the characteristics by the binder, beside the unavoidable reduction in maximum water uptake. The hydrophilic properties of water composite sorbents were improved by the preparation of the silica matrix with smaller mesopores than 10 nm, adding higher amount of hygroscopic salt and by changing the preparation procedure of the composites [37]. Water composite sorbents containing ordered mesoporous silica matrix and different contents of CaCl₂ (4 wt.%, 10 wt.%, 20 wt.%, 30wt%) were prepared by the incipient wetness impregnation. This method preserved the ordered mesoporous structure of the composites. The maximal water capacities increased with higher contents of CaCl₂. The composite sorbents with 20 wt.% of CaCl₂ had the highest maximal water uptake of 2.33 g/g (at 0.94 p/po) and sorbed 0.62 g/g at 0.4 p/po, which is 3 times higher than maximal water uptake of the matrix. The shifts of the water isotherms to lower relative pressure for higher amounts of CaCl₂ were achieved, successfully. Tests of 20 cycles between 40°C and 140°C and a relative humidity of 76%, of all composites showed good hydrothermal stability. The lowest loss of water uptake (1.2%) after 20 cycles showed the composite containing 20 wt% of CaCl₂. And it was 3 times lower than the loss of water uptake of similar composite containing lower amount salt [38], measured under similar conditions. No salt leaching from the matrix was detected after 20 cycles. Regeneration temperatures of the composites were in the range from 120 to 140°C depending on the amount of the salt in the composite.

3. Conclusions

This overview presents selected contributions of researchers involved in the IEA SHC Task 42 / ECES Annex 29 (Task 4229). In the scope of this task from 2013 to 2015 more than 20 institutions from more than 12 countries were taken part in working group A1: "Engineering and processing of TES materials". During this period different new and improved PCMs and TCMS were synthesized. The physical and structural properties of these materials were determined, cycling and thermal stability was studied and the role of material containers (corrosion issues) was analyzed. New low-cost PCMs coming from waste, by-products and natural resources have been produced. Most promising ones have latent heat between 200-300 J/g and can cover TES applications at 50°C-70°C. New eutectic mixtures of linear alkanes with saturated fatty acids or monohydrated alcohols were also obtained and proved to be an efficient way for adjusting the melting point while preserving enthalpy values. New sugar alcohol based eutectic mixtures lowering the original high temperature of single materials were produced. They proved to have high latent heat (240-300 J/g), proper melting point (75-87°C) for solar heating and DHW applications, and evident subcooling effect which enable low-cost long-term storage schemes. Sugar alcohols for TES in industrial applications at higher

temperatures (100-200°C) were also investigated and proved to have high compactness potential. Among TCMs new sorbent water composites containing CaCl_2 within porous silica were prepared for low temperature heat transformation applications. Binder-free zeolite X was used for a seasonal compact thermal adsorption storage and zeolite Y was dealuminated for adsorption heat pumps for low temperature utilization ($T < 100^\circ\text{C}$). Salt hydrates were impregnated into porous carbon and vermiculite in order to improve cycling stability. Different optimal methods for materials processing were also found, like microencapsulation (caprylic acid/chitosan-gelatine), micro/nanoencapsulation (capric, lauric and myristic acids with polystyrene shell), phase-change slurries (n-octadecane-water emulsion) for PCMs and new combinations of composite materials (PCMs and TCMs). TCM composites were prepared by impregnation (MgCl_2 /porous carbon or vermiculite, APO/carbon) and incipient wetness impregnation (CaCl_2 /porous silica). Improvements of TCM's properties were achieved by the oxidation treatment of activated carbon, composites of CaCl_2 /porous silica and binder-free zeolites X and Y (hydrophilicity), dealumination of zeolite Y (lower regeneration temperature), preparation of APO/carbon composite or APO coating on metal plate (thermal conductivity), mixing MgCl_2 and CaCl_2 (preservation of cycling stability), etc. The research was mainly conducted in the field of PCMs, while only few researches were performed in the field of thermochemical materials. It can be observed that mainly engineers/physicists were involved in the research of materials and there were very few chemists. In the future, experts of material science and chemists from the fields of organic and inorganic chemistry should be more involved in order to strengthen the development of TES materials.

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