



# INORGANIC SALT HYDRATES AS PHASE CHANGE MATERIALS (PCM) FOR THERMAL ENERGY STORAGE IN SOLAR INSTALLATIONS

## NIEORGANICZNE HYDRATY SOLI JAKO MATERIAŁY ZMIENNOFAZOWE (PCM) DO MAGAZYNOWANIA ENERGII CIEPLNEJ W INSTALACJACH SŁONECZNYCH

Marta Styś-Maniara\*, Edyta Nartowska, Monika Metryka-Telka  
Kielce University of Technology, Poland  
Rafał Porowski  
AGH University of Science and Technology, Poland

### Abstract

*The authors present a general idea of using inorganic salt hydrates in solar installations. A key role in this selection is played by thermophysical parameters, so the authors review their test methods and in turn characterize them for the most promising salt hydrates. Next, the authors describe the advantages and disadvantages of inorganic salt hydrates and indicate possibilities for their improvement. The use of salt hydrate converters in PV installations significantly improves the efficiency of photovoltaic modules. We show that at least 18 salt hydrates are promising for solar applications with the best ones being Sodium Hydrogen Phosphate Dodecahydrate, Sodium Carbonate Decahydrate and Calcium Chloride Hexahydrate. The selection of a test method for determining the thermophysical parameters of salt hydrates should be individual depending on the research objective. Comparing the methods presented, we believe that it is the DSC and DTA methods that provide the most accurate and repeatable results.*

**Keywords:** salt hydrates, phase change materials, thermal energy storage, latent heat storage

### Streszczenie

*Autorzy przedstawiają ogólną koncepcję wykorzystania nieorganicznych hydratów solnych w instalacjach solarnych. Kluczową rolę w tym doborze odgrywają parametry termofizyczne, dlatego autorzy dokonują przeglądu metod ich badania i kolejno charakteryzują je dla najbardziej obiecujących hydratów solnych i ich mieszanin. Następnie autorzy opisują zalety i wady nieorganicznych hydratów solnych oraz wskazują możliwości ich udoskonalenia. Zastosowanie konwerterów hydratów solnych w instalacjach PV znacząco poprawia sprawność modułów fotowoltaicznych. Wykazano, że co najmniej 18 hydratów soli i ich mieszanin jest obiecujących dla zastosowań solarnych ze względu na korzystne parametry termofizyczne, przy czym najlepsze z nich to dodekahydrat wodorofosforan sodu, dekahydrat węglanu sodu i heksadydrat chlorku wapnia. Z przeglądu literatury wynika, że wybór metody badawczej do określenia parametrów termofizycznych hydratów soli powinien być indywidualny w zależności od celu badań. Porównując przedstawione metody, stwierdzono, że to właśnie metody DSC i DTA dają najbardziej dokładne i powtarzalne wyniki.*

**Słowa kluczowe:** hydraty soli, materiały zmiennofazowe, magazynowanie energii cieplnej, magazynowanie ciepła utajonego

## 1. INTRODUCTION

Consumption of fossil fuels and carbon dioxide is increasing. An energy crisis is on the horizon, legislative standards for environmental disturbance are becoming stricter. In addition, public consciousness is growing and people are moving towards sustainable development. All this is causing the search for alternative energy sources and the continuous development of energy storage mechanisms. Currently, 3 types of TES systems for physical heat storage are known (Fig. 1).

One example of latent heat storage is PCM materials. Latent heat can be stored during the phase transformation of a given material and released under suitable conditions. It is divided according to the type of phase transformation (liquid-solid, solid-liquid and solid-solid). Within the solid-liquid interactions there are compounds:

- organic (waxes, paraffinic-alkane compounds, non-paraffinic compounds, fatty acids, alcohols, ionic liquids);
- inorganic (salts, hydrates-hydrated salts, metals, metal hydrides);

- eutectic mixtures (organic-organic, inorganic-inorganic, inorganic-organic) [1].

The use of PCMs helps to manage energy efficiently. The potential of these materials caused a rapid development of research in their direction in recent years, especially when it comes to salt hydrates [2, 3].

Inorganic salt hydrates, which are a large part of PCMs, have always attracted interest due to their affordable price, good thermal conductivity and high energy storage density. However, disadvantages such as leakage, supercooling and phase separation limit their practical application [4-6]. To reduce these disadvantages, PCMs of stable form have been tested by incorporating PCMs into porous materials or by microencapsulation to prevent leakage and phase separation [7-9]. Research is still being undertaken to improve salt hydrates for specific applications. In order to fully realize the potential of salt hydrates as PCM materials in solar installations, it is necessary to better understand their possibilities and limitations for such solutions.

The authors present a general idea of using inorganic salt hydrates in solar installations. A key

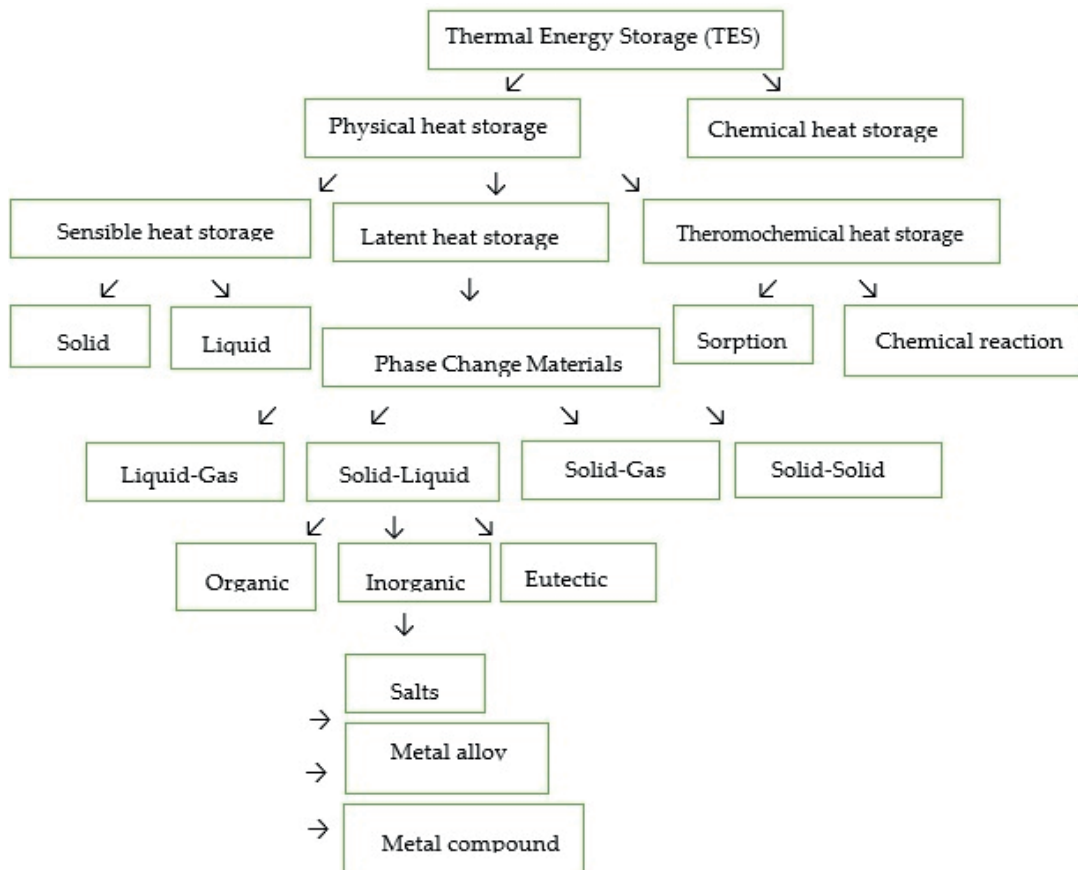


Fig. 1. Classification of thermal energy storage technologies [1]

role in this selection is played by thermophysical parameters, so the authors review their test methods and in turn characterize them for the most promising salt hydrates and their mixtures. Next, the authors describe the advantages and disadvantages of inorganic salt hydrates and indicate possibilities for their improvement. Finally, the authors provide directions for future research necessary to select a suitable inorganic salt hydrate for solar applications.

## 2. SALT HYDRATES AS PCM MATERIALS IN SOLAR INSTALLATIONS

Solar energy can be collected directly into electricity using a photovoltaic (PV) module. However, when solar radiation arrives at the PV module, it is not only converted into electricity, but also into thermal energy, which increases the temperature of the PV system. There are many factors that affect the output of a PV system [1].

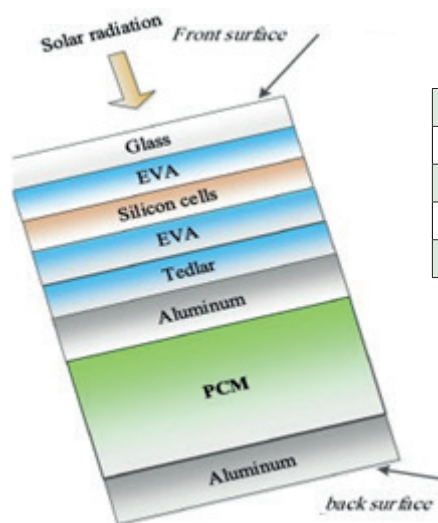
One of them is temperature. The efficiency of a PV module is the inverse of temperature. According to the Standard Test Conditions, if a PV module operates at a temperature higher than the ambient temperature, 25°C, then for every one degree Celsius increase in temperature, the conversion rate of the PV module drops as low as 0.5%. Summer is the season with the highest solar radiation. Daytime temperatures in summer are typically between 40°C and 70°C, which is 2-3 times the ideal operating temperature of solar panels. This puts the overall efficiency of the PV system at risk – a potential drop in conversion factor of (7.5-22.5)%. Overheating of PV modules finally shortens their lifetime ( $x, y$ ). A simple solution to reduce the surface temperature of the current PV system is to cool (by convection) the back of the PV panels by using a phase change material (PCM). PCMs are materials that go through reversible stages that depend on their temperature. They can accept or reject heat. The principle of PCM in a PV module is simple. Excess heat from the panel surface caused by an increase in ambient temperature will be consumed by the attached PCM, until the physical phase of the PCM is completely transformed (e.g., from solid to liquid). As the panel temperature drops, the PCM solidification process should release heat to the working fluid in the PV panel, to the structure, or will act as an insulator in the system. Solutions using PCM in solar installations are well-known in the scientific community.

Karthick et al. [9] integrated Glauber salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) into a photovoltaic system for the

façade of a test building in India. The purpose of the study was to evaluate the improvement in electrical and thermal energy results. Glauber's salt was encapsulated with a sheet of tedlar and then attached right behind each polycrystalline PV cell. To make a single module (Building Integrated Photovoltaics) BIPV, the cells were placed between additional low-iron glass materials. Output power and efficiency were analyzed and the orientation of the module and test room were taken into account to evaluate solar heat gain through the facade. The results showed a 10% increase in electrical output with the PCM. This was due to an 8°C reduction in the system's instantaneous peak temperature. The overall PV cell temperature decreased by 12% [9]. Another BIPV-related study was conducted by Hasan et al. [10]. In this experiment, calcium chloride hexahydrate ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ) was tested in 4 different PV-PCM systems. The tests were conducted at low as well as high solar irradiance, in order to fully evaluate the efficiency of the system. Polycrystalline silicon photovoltaic cells with Perspex as a housing were placed on the front of four containers made of different materials. The materials and sizes of the system's containers were carefully selected to study the effects of thermal conductivity (for system A and C made of aluminum) and insulation (for system B and D made of perspex), wall thickness and thermal mass of the PCM on temperature control. While the ambient temperature remained constant ( $\sim 20^\circ\text{C} \pm 1^\circ\text{C}$ ), the results showed that calcium chloride hexahydrate lowered the cell temperature at solar irradiance  $>750 \text{ W/m}^2$ , increasing the temperature deviation time. In the BIPV-PCM system, at  $750 \text{ W/m}^2$ , the PV cell surface temperature decreased to 18°C, and the constant temperature was maintained for about 30 minutes. In contrast, at  $1000 \text{ W/m}^2$ , although the reduction in surface temperature was smaller (10°C), the duration increased to 5 hours.

The studies presented above show the suitability of inorganic salt hydrates as PCM materials to improve the efficiency of PV systems. Similarly, Hussein et al. [11] investigated a PV/PCM system with a crystalline silicon panel as the electrical component, a rectangular aluminum chamber filled with PCM as the thermal component (Fig. 2). It was assumed that the aluminum chamber is in ideal thermal contact with the PV panel.

By changing the components in a PV/PCM system, heat can be generated for useful use. The authors observed improvements in all parameters. Combining



Parameter	Glass	EVA*	Silicon cells	Tedlar	Al. chamber
Thermal conductivity (W/mK)	1.04	0.3	148	0.2	202
Density (kg/m <sup>3</sup> )	2500	935	2330	1500	2791
Specific heat capacity (J/kgK)	750	2500	700	1090	871
Thickness (mm)	3.2	0.5	0.2	0.5	5

\*ethylene-vinyl acetate

Fig. 2. Cross-section of the PV-PCM system and basic properties of the system layers [11]

the properties of all layers including glass, EVA, silicon cells, tedlar and PCM gives us a cell with better specific heat capacity, better density and higher thermal conductivity.

### 3. METHODS FOR STUDYING THE THERMOPHYSICAL PROPERTIES OF SALT HYDRATES

The main thermophysical parameters of salt hydrates include *melting point, heat of fusion and density*.

#### 3.1. Melting point and heat of fusion – assumptions of research methods

Chemical substances undergo a variety of physical and chemical transformations due to changes in ambient temperature. In the case of pure substances, these transformations allow for effective identification of their chemical structure, and the study of mixtures allows for their qualitative and quantitative analysis. Among the most commonly studied temperature-dependent physical transformations are:

- melting/solidification – that is, a change in the solid/liquid state of phase. It is a characteristic of pure chemicals having a crystalline structure (both inorganic and organic);
- change in specific gravity – shown by a change in the volume of a liquid substance or a change in the dimension of a solid (contraction or dilation).

Calorimetry is one of the most precise and convenient methods of studying solids by determining their specific heat as a function of temperature, phase transitions of various types, phase diagrams. Calorimeters are used to qualitatively evaluate exo-

and endothermic processes, as well as to quantify the progress of a reaction. Frequently used thermal analysis methods include differential tests [12].

**Differential Scanning Calorimetry (DSC)** relies on the measurement of the difference between the heat flow vs. temperature relation of the sample and the heat flow vs. temperature relation of a standard. Directly measured signal is a change in temperature between a test sample and a reference sample (Fig. 3). This difference is proportional to the flow of the heat flux between the two samples and is automatically converted to the value of the heat flux using special software. The result of calorimetric measurements is a DSC curve shown as the temperature dependence on the heat flux, an endo- and exothermic peaks are recorded on these curves, which result from the temperature differences between a tested sample and a reference sample. The measurements are performed in the controlled inert gas atmosphere of high purity (nitrogen). In shape, the DSC curve shows good agreement with the DTA curve. On the DSC curve we can distinguish sections of the so-called baseline, which are shifted parallel to the temperature axis by a certain small value of dH. They mark the temperature intervals in which no processes related to heat release or absorption take place in the sample. When a reaction or phase transformation occurs, the baseline turns into a peak. This is the part of the curve where it deviates from the baseline and then returns to it. An endothermic peak occurs when the temperature of the test sample is lower than the reference sample, while an exothermic peak occurs when the temperature of the test sample rises



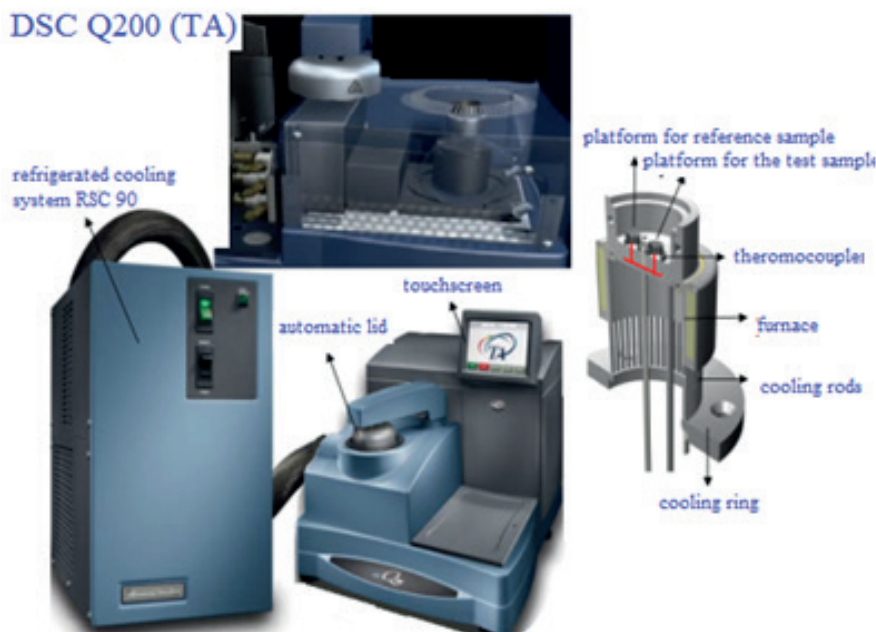


Fig. 3. DSC Q200 (TA Instruments)[own study]

above the temperature of the reference sample. In the first case, heat must be supplied to the test sample (downward-oriented peak), while in the second case, heat is received by the system (upward-oriented peak) [14].

**Differential Thermal Analysis (DTA)** is a method where the temperature difference between a test substance and a reference substance is recorded as two samples in a controlled heated or cooled environment.

The result of the measurement is a DTA curve, which is the temperature difference as a function of temperature or time [13]. One of the instruments for DTA testing is the SDT Q600 (Fig. 4).

**The T-history method** is based on comparing the history of temperature change over time for a phase change material and a reference material. Analysis of the temperature distribution allows the values of melting point, specific heat and enthalpy of fusion of

**Pure Gas System**  
Field-proven, horizontal purge gas system. Dual digital mass flow controllers and gas switching capability Inconel® reactive gas inlet. Easily interfaced to a MS or FTIR. Better baselines with minimum buoyancy effects

**Thermobalance**  
Accurate and reliable horizontal dual-balance. Supports both DSC and TGA measurements. Weight signal is the differential between the sample and reference beams. Less drift compared to single-beam designs. Independent TGA measurements on two samples simultaneously.

**Furnace**  
Rugged, bifilar-wound, horizontal furnace. Accurate and precise heating rate ramps and isothermal operation. Smooth automatic furnace opening / closing. Easy sample loading. Rapid post-experiment furnace cool-down.

**Temperature Control & Measurement**  
Platinum / Platinum-Rhodium thermocouple pair. Direct sample, reference, and differential temperature from ambient to 1,500 °C. Superior ΔT accuracy compared to single-beam designs. True differential heat flow signal. Superior baseline performance.

Fig. 4. SDTQ600 [TA Instruments.com]

the PCM material to be obtained [16]. The smallest differences in results are observed at the melting temperature.

When determining thermophysical parameters for mixtures, the so-called *Dynamic method* is practiced. It allows the measurement of liquid-solid and liquid-liquid phase equilibria. Measurements involve visual observation of the temperature of disappearance of the last solid-phase crystal (SLE) or disappearance of opacity (LLE) at a controlled heating rate. A diagram of the apparatus used is shown in Figure 5. In practice, the determination of phase diagrams is performed as follows. A small amount of salt hydrate is introduced into the measuring flask, followed by another hydrate. Each time the flask is weighed before and after the addition of the second salt hydrate. A volumetric flask with a mixture of a well-defined composition (1 x) is placed in a water bath. The contents of the flask are slowly heated with an electric heater connected to an autotransformer, which provides precise regulation of the heating rate.

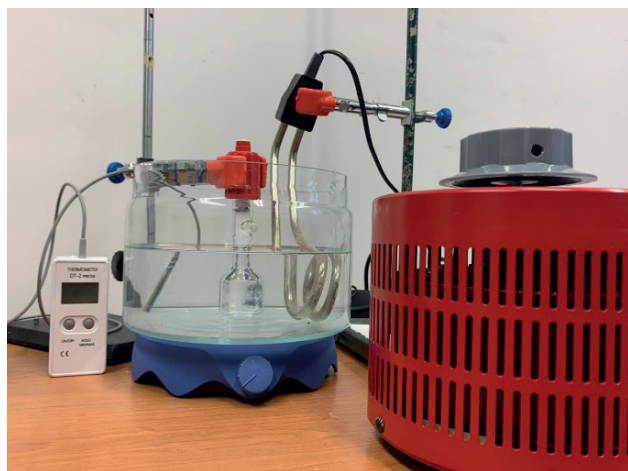


Fig. 5. Apparatus for measuring phase equilibria by dynamic method: electronic thermometer; measuring vessel; electric heater; Teflon-coated magnetic stirrer; stirring element for heating or cooling medium in bath; water, oil or acetone bath; magnetic stirrer [own study]

Under strong light passing through the test sample, the temperature of the disappearance of the last crystal or the disappearance of the opacity is observed. The temperature of the system is measured using a thermometer whose probe has been completely immersed in a water bath. The accuracy of the temperature measurement is estimated at  $\pm 0.01$  K. During the measurement, both the sample was subjected to continuous stirring using a magnetic and mechanical stirrer, which makes it possible to

eliminate concentration and temperature gradients within them [17].

### 3.2. Melting point and heat of fusion – limitations of methods when testing salt hydrates

DSC is a common instrument in most PV-PCM system performance studies. The quality of the DSC curve depends on many factors. The most important of these are *the mass of the sample, the rate of temperature change used and the positioning of the substance in the vessel*. The optimal mass of the test sample is usually between a few and a dozen milligrams. The greater the mass of the sample, the greater the observed thermal effect. If weak thermal effects are observed, a higher mass should be used. However, when the test substance exhibits closely spaced anomalies, the use of a large mass can cause them to combine into a single anomaly on the DSC curve. The rate of temperature change, can be selected depending on a number of factors. Typically, measurements are made at a rate of 5 or 10 K/min. An increase in the heating rate results in an increase in the size of the anomalies with a simultaneous broadening of the anomalies. Uniform distribution of substances in the vessel ensures good heat transfer and, consequently, correct temperature indications of the phase transitions or chemical reactions taking place [18].

According to some authors, the expensive DSC method may not be suitable for PCM testing because DSC uses only about 10 mg of sample mass [15]. This creates difficulties in determining the problems associated with larger samples during phase isolation, dispersion, high supercooling, etc. during the study. Finally, small sample sizes in testing are usually not indicative of real engineering systems or industrial applications that require huge amounts of PCMs, especially for heterogeneous materials. As a result, the authors [15] believe that other techniques should be considered that allow for larger test sample weights in a study, such as the T-History method. The THM method provides a simple experimental device, the ability to simultaneously measure the melting point, specific heat and thermal conductivity of several PCM samples, and the possibility to observe the phase transformation process of each PCM sample [19]. The major disadvantage may be the inaccuracy of the results. Conducting T-history tests requires special care on the part of the investigator. During the test, it is necessary to watch out for two main factors that have determined significant measurement errors:

inaccuracy of the temperature measurement reading and movement of the thermocouple in the sample during the measurement, which directly affect the decrease in measurement accuracy [19].

For the dynamic method, the experiment is labor-intensive and subject to error, as crystallization from solution was a very difficult and slow process. The method, has been known for more than 100 years, where it was commonly used to determine solubility curves. It allows detailed observation of the full range of molar fractions of the solute. It is a largely subjective method and requires a great deal of feeling on the part of the experimenter.

The literature review shows that the selection of a test method for determining the thermophysical parameters of salt hydrates should be individual depending on the research objective. Comparing the methods presented, we believe that it is the DSC and DTA methods that provide the most accurate and repeatable results.

### 3.3. Density

The pycnometer method is one of the simplest methods to determine density. The instrument consists of a container of a certain volume and a sealed lid with an opening for the excess liquid under test to flow out. The vessel is weighed before and after filling. Density is calculated as the ratio of the weight of the product to the volume of the pycnometer (Fig. 6).

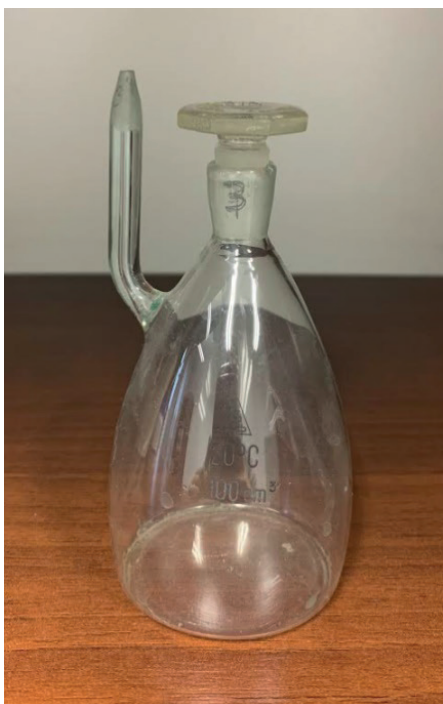


Fig. 6. Pycnometer [own study]

## 4. THE CHARACTERISTICS OF SALT HYDRATES AND THEIR MIXTURES

### 4.1. Thermophysical properties

Salt hydrates are described by the general formula  $AB - nH_2O$ , where  $n$  is the number of water molecules,  $AB$  indicates the composition of the salt. During the phase transformation, the salt undergoes dehydration [23]. The thermophysical properties of salt hydrates are an important parameter when evaluating these substances. They can regulate the temperature of photovoltaic cells and improve the electrical performance of photovoltaic panels in different temperature environments [24].

In Thermal Energy Storage (TES) systems, usable energy is transferred from the solar collector to the medium (PCM) as sensible or latent heat. Latent heat is most attractive because it has a higher density, so the required volume of material is smaller than for sensible heat storage [25]. Latent heat uses the phase transformation material as the storage medium. When the temperature increases, the phase transformation occurs and the material changes from a solid to a liquid state, absorbing heat and thus compensating for the temperature increase. In the same manner, when the temperature decreases, the PCM goes from a liquid to a solid state, transferring heat to the medium and thus compensating for the decrease in temperature. Such properties are essential for improving the efficiency of photovoltaic panels [25].

The melting point range of salt hydrates is between  $15^{\circ}\text{C}$  and  $117^{\circ}\text{C}$  [26]. They are characterized by high heat capacity and high latent heat of  $330\text{ kJ/kg}$  [27], high thermal conductivity and low price. Depending on the phase transformation efficiency, salt hydrates can be divided into three categories: salt hydrates with congruent, incongruent and semi-congruent melting properties. Many salt hydrates that process a high latent heat transition and a moderate phase transformation temperature do not have congruent melting properties. The phase transformation temperature range of a single salt hydrate may not always fit practical applications. Therefore, two or more salt hydrates can be mixed to adjust the melting temperature. Salt hydrate mixtures can be divided into eutectic mixtures with congruent behavior and non-eutectic mixtures with incongruent melting points. Eutectic mixtures usually do not segregate during melting and freezing because they freeze to form crystalline mixtures [28-31]. Multi-component eutectic mixtures with a common melting point and high latent heat can lower the melting point

of a single-component salt hydrate, and can then be used in broader fields [32]. In addition, eutectic mixtures can also eliminate the disadvantages of single salt hydrates, including supercooling and phase separation. Liu et al. [33] described eutectics of hydrated salts  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  to find applications in thermal energy storage in solar systems. The eutectics showed no phase separation and the degree of supercooling was reduced [33]. It was found that the inclusion of eutectic PCM improved the efficiency by 12% and lowered the module temperature by  $12^\circ\text{C}$  compared to a conventional PV module. Xin et al. [34] determined the optimal ratio of nucleating and thickening agents to reduce the level of supercooling and eliminate phase separation in a binary mixture of eutectic  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ .

Inorganic salt hydrates that can be required for solar applications along with their thermophysical parameters are summarized in Table 1.

Higher values of energy storage density translate into a smaller volume of material required to

accumulate a given amount of heat. The best compounds considering heat of fusion to density relationship are Sodium Hydrogen Phosphate Dodecahydrate, Barium Hydroxide Octahydrate and Magnesium Sulfate Heptahydrate. The use of these substances will provide a relatively small converter giving a large enough heat of fusion.

## 4.2. Advantages and disadvantages

Phase change materials should have properties that are difficult to achieve simultaneously. PCMs absorb, store and release large amounts of energy in the form of latent heat at a constant temperature, which is called the phase change temperature. Such a transformation is an isothermal transformation, that is, the amount of heat stored during the heating of any material is significantly less than the amount of heat accumulated during the phase transformation of that material [9]. Phase-change materials are characterized by properties [4]:

- **Physical** (high density, low density variation during phase transformations, low vapor pressure, no supercooling effect, moderate crystallization rate, low viscosity);

Table 1. Thermophysical properties of salt hydrates and their eutectics

Chemical formula	Heat of fusion (J/g)	Density (Solid) (g/cm <sup>3</sup> )	Melting point (°C)	References
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ Sodium Hydrogen Phosphate Dodecahydrate	280	1.71	35-44	[5]
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ Barium Hydroxide Octahydrate	266	2.18	78	[31]
25% $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ + 75% $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	262.3	n/a	31.2	[34]
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ Sodium Sulfate Decahydrate	248	1.46	32.4	[31]
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ Sodium Carbonate Decahydrate	247	1.44	33	[31]
40% $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ + 60% $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	220.2	n/a	27.3	[33]
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ Sodium Thiosulfate Pentahydrate	201/206	1.73	48	[23]
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ Magnesium Sulfate Heptahydrate/Epsom salt	202	2.66	48.5	[23]
$\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ Magnesium Chloride Tetrahydrate	178	1.57	58	[32]
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ Calcium Chloride Hexahydrate	174	1.8	28	[32]
$\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ Copper Sulfate Heptahydrate	171	2.28	40.7	[23]
53% $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ + 47% $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	168	n/a	66	[32]
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ Magnesium Nitrate Hexahydrate	163	1.46	89.9	[32]
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ Aluminium Nitrate Nonahydrate	155	1.058	72	[2]
50% $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ + 50% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	132	n/a	58-59	[32]
75% $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ + 25% $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	102.3	n/a	21.4	[32]
$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ Calcium Chloride Tetrahydrate	99.6	1.566	44.2	[32]
$\text{K}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ DiPotassium Hydrogen Phosphate Heptahydrate	99	1.52	48	[33]



- **Thermal** (proper phase transformation temperature range adapted to the operating temperature of the PV plant, high latent and specific heat and high thermal conductivity of both phases);
- **Chemical** (non-combustible, non-explosive, non-toxic, recyclable, no chemical decomposition);
- **Economic** (available in large quantities, cost-effective during application).

When used for solar installations, inorganic salt hydrates show advantages and disadvantages (Table 2).

Table 2. Advantages and disadvantages of inorganic phase change materials [25]

Inorganic salt hydrates as PCM materials	
Advantages	Disadvantages
High phase change energy	Chemically unstable
High capacity and thermal conductivity	May cause corrosion
Easily available	Supercooling
Non-combustible	Phase separation
Price	

**The advantage** is the high heat capacity of the phase change. Thanks to it, PCM materials have the ability to accumulate heat. Also very important in the operating conditions of PCMs is the enthalpy change associated with supercooling or overheating of these materials (hysteresis of the phase transformation), which is a few to several degrees with regard to the melting point. A high value of thermal conductivity provides materials with a more efficient absorption or release of heat between the system and the environment, even for small temperature differences [2]. When a substance does not achieve such a condition, techniques are used to increase the effective thermal conductivity, usually by adding well-conducting materials such as graphite [37]. The economic advantages of PCMs include the low price of these materials [2]. Inorganic materials are described as non-combustible [23]. Inorganic salt hydrates are flexible materials. Even the seemingly good characteristics included as advantages can be improved. Duan et al. [43] prepared composites of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and EG by adsorbing liquid salt hydrates onto EG. A stably shaped composite was obtained by introducing EG into molten  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . In addition, polyoxyethylene-10 alkylphenols were added as an emulsifier to increase the bonding strength between EG and salt hydrate. Thermal conductivity was improved by 82% compared to pure  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . Cui et al [53] used vacuum impregnation to prepare a compound of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  and sepiolite. This fibrous clay mineral proved to be a good flame retardant

and can be widely used in buildings. The resulting  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  composite provided good phase change energy storage performance, but sepiolite reduced enthalpy and thermal stability.

**The disadvantages** of hydrated salts are the supercooling effect and phase separation problems. These two phenomena are closely related, due to the different densities of water and salt. Thus, during crystallization of hydrated salts, which have a complex structure, a solid-phase sediment is formed in water, which does not have the ability to accumulate heat [36]. Phase separation is a significant problem associated with salt hydrates [37]. A way to minimize and avoid phase separation is to add thickeners to salt hydrates. Thickeners that have been studied include hydroxyethyl cellulose, nanocellulose, cellulose [38-41], polyethylene glycol [42] and some silicone derivatives [43]. Fine-grained auxiliary materials for inorganic materials include such porous materials as expanded graphite [44], diatomaceous earth [45] and titanium nanodioxide [46]. They increase the viscosity of the solution, which allows for uniform distribution of the solids. Effective methods include microencapsulation and microencapsulation combined with impregnation using porous materials. They solve phase separation problems, but can also effectively avoid leakage during PCM synthesis.

Microencapsulated phase transition materials (MEPCMs) typically consist of a polymeric material as the shell and a PCM as the core [47]. Microencapsulated salt hydrates can change reactivity with the external environment. They can be used as a powder and then prevent phase separation and PCM leakage. The microcapsules showed excellent performance, with no leakage or phase separation. PCM microcapsules consisting of  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  as the core and methyl methacrylate as the capsule were prepared by Huang et al. [48]. They used a suspension copolymerization method with a volatile solvent. In the polymerization reaction, the primary salt hydrate  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  lost five water molecules during heating, while the rest were successfully diverted to the organic solvent. The thermal conductivity seemed to remain unchanged after the formation of the  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  microcapsule. Thus, it can be considered a potential material for solar space heating.

Porous materials such as carbon foam, diatomaceous earth, expanded graphite and expanded perlite used as support materials can also effectively eliminate the leakage, phase separation and corrosion problems of PCM. Such composite materials are often synthesized

by impregnating PCMs or mixing them with a porous matrix [49]. Supporting materials with large specific surface areas cause liquid materials to be absorbed through their internal pores. Expanded graphite (EG) is a type of carbon material formed by annealing graphite at high temperatures using microwave radiation. Good performance characterizes EG and PCM with high thermal conductivity, low weight, no phase separation leakage and low overcooling due to expanded graphite capillary and surface tension [50-53].

Pichandi et al. considered eutectic PCM by adding magnesium sulfate heptahydrate 30% ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) to sodium carbonate decahydrate 70% ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ), to eliminate the problems of supercooling and phase separation of sodium carbonate in PV. Through a DSC study, it was found that this substrate content tends to perform best in terms of thermal conductivity and stability, latent heat of fusion, melting point. This eutectic PCM was placed on the back of a 25 W polycrystalline silicon PV module. The experiment was conducted on two specific days selected based on outdoor solar conditions in India. Equipment including a temperature data logger, voltmeter, ammeter, solar radiation sensor and thermoelectric wire were used to evaluate the performance of the PV- PCM system. According to the collected data, the system showed a maximum temperature drop of  $7^\circ\text{C}$ , resulting in a 1.21% increase in efficiency. The power output of the system was 17.63 W higher with the eutectic PCM, which improved power production by 12.5%. However, when comparing the cost of this PV- PCM system to the monetary return in the long term, there is very little or no economic benefit, as PCM material preparation and setup cost extra, even in mass production. Therefore, various salt hydrates with similar properties to magnesium sulfate heptahydrates are potential substitutes for this study [9].

Phase-change materials can cause corrosion, then, if the inappropriate tank in which this PCM will be

stored is selected. Brass, copper and aluminum are avoided. Glass, polypropylene and stainless steel are good candidates as PCM carriers for long-term storage of PCM salt hydrates [1].

There is no salt hydrate that has the advantages alone. In practice, the choice of material is made on the basis of the amount of heat capacity and phase change temperature, as well as price. Disadvantages of the material are eliminated or reduced by various physical procedures (e.g., using stabilizing additives and nucleators) or by designing the system accordingly [3].

## 5. CONCLUSIONS

In the article, we highlight the important role played by salt hydrates in PV installations. The use of salt hydrate converters in PV installations significantly improves the efficiency of photovoltaic modules. We show that at least 18 salt hydrates and their mixtures are promising for solar applications due to their beneficial thermophysical parameters with the best ones being Sodium Hydrogen Phosphate Dodecahydrate, Sodium Carbonate Decahydrate and Calcium Chloride Hexahydrate. The literature review shows that the selection of a test method for determining the thermophysical parameters of salt hydrates should be individual depending on the research objective. Comparing the methods presented, we believe that it is the DSC and DTA methods that provide the most accurate and repeatable results.

Salt hydrates have many advantages and disadvantages that are well known in the scientific community. In this paper we show that inorganic salt hydrates are flexible materials and in addition to the disadvantages even the seemingly good characteristics included as advantages can be improved. Research is still needed to assess the potential for changes in the individual properties of salt hydrates during long-term operation of solar systems, which can influence the efficiency of the solar system.

## REFERENCES

- [1] Singh G.K.: *Solar power generation by PV (photovoltaic) technology: A review*, Energy 2013, 53, pp. 1-13.
- [2] Cabeza L.F., Castell A., Barreneche C.D., de Gracia, A., Fernández A.: *Materials used as pcm in thermal energy storage in buildings: a review*, Renew. Sustain. Energy rev. 2011, 15, pp. 1675-1695.
- [3] Li T.X., Wu D.L., He F., Wang R.Z.: *Experimental investigation on copper foam/hydrated salt composite phase change material for thermal energy storage*, Int. J. Heat mass transf. 2017, 115, pp. 148-157.
- [4] Kenisarin M., Mahkamov K.: *Salt hydrates as latent heat storage materials: thermophysical properties and costs*. Sol. Energy Mater. Sol. Cells 2016, pp. 145, 255-286.
- [5] Zhang P., Xiao X., Ma Z.: *A review of the composite phase change materials: fabrication, characterization, mathematical modeling and application to performance enhancement*, Appl. Energy 2016, 165, pp. 472-510.

- [6] Raj B., Van de Voorde M., Mahajan Y.: *Phase change nanomaterials for thermal energy storage*. In nanotechnology for energy sustainability, 2017, pp. 459-484.
- [7] Wang T., Wang S., Luo R., Zhu C., Akiyama T., Zhang Z.: *Microencapsulation of phase change materials with binary cores and calcium carbonate shell for thermal energy storage*. Appl. Energy 2016, 171, pp.113-119.
- [8] Giro-Paloma J., Martínez M., Cabeza L.F., Fernández A.I.: *Types, methods, techniques, and applications for microencapsulated phase change materials (MPCM): A review*. Renew. Sustain. Energy Rev. 2016, 53, pp. 1059-1075.
- [9] Choo Y.M., Wei W.: *Salt hydrates as phase change materials for photovoltaics thermal management*. Energy Science & Engineering, 2021, 10, pp. 1630-1645.
- [10] Hasan A., McCormack S.J., Huang M.J., Norton B.: *Evaluation of phase change materials for thermal regulation enhancement of building integrated photovoltaics*, Solar Energy, 2010, 84, pp. 1601-1612.
- [11] Taqi Al.-Najjar H.M., Mahdi J.M.: *Novel mathematical modeling, performance analysis, and design charts for the typical hybrid photovoltaic/phase-change material (PV/PCM) system*, Applied Energy, 2022, 315, 119027.
- [12] Zielenkiewicz W.: *Calorimetry*, Inst. of Phys. Chem. of Polish Acad. of Sciences. 2005.
- [13] Shelby J.E.: *Thermal analysis of Glasses. Chapter 12 in Introduction to Glass Science and Technology*. The Royal Society of Chemistry. 2005.
- [14] Pielichowska K., Pielichowski K.: *Różnicowa kalorymetria skaningowa z modulacją temperatury (MT-DSC)*, Laboratorium, 2007, 7-8, pp. 36-38.
- [15] Hasan A., McCormack S.J., Huang M.J., Norton B.: *Characterization of phase change materials for thermal control of photovoltaics using Differential Scanning Calorimetry and Temperature History Method*. Energy Conversion and Management, 2014, 81, pp. 322-329.
- [16] Sole A., Miro L., Barreneche C., Martorell I., Cabeza L.F.: *Review of the T-history method to determine thermophysical properties of phase change materials (PCM)*, Renew. Sustain. Energy Rev. 2013, 26, pp. 425-436.
- [17] Domańska U.: *Thermophysical properties and thermodynamic phase behavior of ionic liquids*, Thermochem. Acta 2006, 448, pp. 19-30.
- [18] Wróbel S., Marzec M.: *Różnicowa kalorymetria skaningowa*, Zakład Inżynierii Materiałów, s. 44.
- [19] Yinping Z., Yi J., Yi J.: *A simple method, the T-history method, of determining the heat of fusion, specific heat and thermal conductivity of phase-change materials*. Meas. Sci. Technol. 1999, 10, 201.
- [20] Yinping, Z., Yi J.: *A simple method, the T-history method, of determining the heat of fusion, specific heat and thermal conductivity of phase-change materials*; Meas Sci. Technol, 10 (3) (1999).
- [21] Hong H., Kim S.K., Kim Y.S.: *Accuracy improvement of T-history method for measuring heat of fusion of various materials*. Int J Refrig, 2004, 27 (4), pp. 360-366.
- [22] Marin J.M., Zalba B., Cabeza L.F., Mehling H.: *Determination of enthalpy-temperature curves of phase change materials with the temperature-history method: improvement to temperature dependent properties*; Meas Sci. Technol, 2003, 14 (2), pp. 184-189.
- [23] Xie N., Huang Z., Luo Z., Gao X., Fang Y., Zhang Z.: *Inorganic salt hydrate for thermal energy storage*, Appl. Sci. 2017, 7, 1317.
- [24] Rezvampour M., Borooghani D., Torabi F., Pazoki M.: *Using CaCl<sub>2</sub>·6H<sub>2</sub>O as a phase change material for thermal regulation and enhancing photovoltaic panels' conversion efficiency: Experimental study and TRNSYS validation*. Renewable Energy, 2020, 146, pp. 1907-1921.
- [25] Ushak S., Gutierrez A., Galleguillos H., Fernandez A.G., Cabeza L.F., Grageda M.: *Thermophysical characterization of a by-product from the non-metallic industry as inorganic PCM*. Solar Energy Materials and Solar Cells, 2015, 132, pp. 385-391.
- [26] Melcer A., Klugmann-Radziemska E., Lewandowski W.M.: *Materiały zmiennofazowe. Właściwości, klasyfikacja, zalety i wady*. Przem. Chem., 2012 7, pp. 1000-1011.
- [27] Zwolińska M., Bogdan A.: *Związki zmiennofazowe w zastosowaniach techniczno-użytkowych i ergonomicznych*. Ergonomia, 2012, 4, pp. 22-25.
- [28] Hussain S.I., Dinesh R., Roseline A.: *Enhanced thermal performance and study the influence of sub cooling on activated carbon dispersed eutectic PCM for cold storage applications*. Energy Build. 2017, 143, pp. 17-24.
- [29] Pielichowska K., Pielichowski K.: *Phase change materials for thermal energy storage*. Prog. Mater. Sci. 2014, 65, pp. 67-123.
- [30] Khan Z., Khan Z., Ghafoor A.: *A review of performance enhancement of PCM based latent heat storage system within the context of materials, thermal stability and compatibility*. Energy Convers. Manag. 2016, 115, pp. 132-158.
- [31] Lorente S., Bejan A., Niu J.L.: *Construal design of latent thermal energy storage with vertical spiral heaters*. Int. J. Heat Mass Transf. 2015, 81, pp. 283-288.
- [32] Li G., Zhang B., Li X., Zhou Y., Sun Q., Yun Q.: *The preparation, characterization and modification of a new phase change material: CaCl<sub>2</sub>·6H<sub>2</sub>O–MgCl<sub>2</sub>·6H<sub>2</sub>O eutectic hydrate salt*. Sol. Energy Mater. Sol. Cells 2014, 126, pp. 51-55.



- [33] Liu Y., Yang Y.: *Preparation and thermal properties of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} / \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  eutectic hydrate salt as a novel phase change material for energy storage*. Applied Thermal Engineering 2006, 10, pp. 606-609.
- [34] Xin W., Fang J., Jiang W., Ping L., Na L., Yanhan F., Wang L.: *Preparation and modification of novel phase change material  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} / \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  binary eutectic hydrate salt*. Energy Sources, Part A: Recovery, Utilization and Environmental Effects, 2019, pp. 1-12.
- [35] Mohamed S.A., Al-Sulaiman F.A., Ibrahim N.I., Zahir M.H., Al-Ahmed A., Saidur R., Yılbaş B.S., Sahin A.Z.: *A review on current status and challenges of inorganic phase change materials for thermal energy storage systems*. Renew. Sustain. Energy Rev. 2017, 70, pp. 1072-1089.
- [36] Dannemand M., Johansen J.B., Furbo S.: *Solidification behavior and thermal conductivity of bulk sodium acetate trihydrate composites with thickening agents and graphite*. Sol. Energy Mater. Sol. Cells 2016, 145, pp. 287-295.
- [37] Shin H.K., Park M., Kim H.-Y., Park S.-J.: *Thermal property and latent heat energy storage behavior of sodium acetate trihydrate composites containing expanded graphite and carboxymethyl cellulose for phase change materials*. Appl. Therm. Eng. 2015, 75, pp. 978-983.
- [38] Li Y., Yu S., Chen P., Rojas R., Hajian A., Berglund L.: *Cellulose nanofibers enable paraffin encapsulation and the formation of stable thermal regulation nanocomposites*. Nano Energy 2017, 34, pp. 541-548.
- [39] Hu X., Huang Z., Yu X., Li B.: *Preparation and thermal energy storage of carboxymethyl cellulose-modified nanocapsules*. BioEnergy Res. 2013, 6, pp. 1135-1141.
- [40] Jin X., Medina M.A., Zhang X., Zhang S.: *Phase-change characteristic analysis of partially melted sodium acetate trihydrate using DSC*. Int. J. Thermophys. 2014, 35, pp. 45-52.
- [41] Gutierrez A., Ushak S., Galleguillos H., Fernandez A., Cabeza L.F., Grágeda M.: *Use of polyethylene glycol for the improvement of the cycling stability of bischofite as thermal energy storage material*. Appl. Energy 2015, 154, pp. 616-621.
- [42] Kazemi Z., Mortazavi S.M.: *A new method of application of hydrated salts on textiles to achieve thermoregulating properties*, Thermochim. Acta 2014, 589, pp. 56-62.
- [43] Duan Z.-J., Zhang H.-Z., Sun L.-X., Cao Z., Xu F., Zou Y.-J., Chu H.-L., Qiu S.-J., Xiang C.-L., Zhou H.-Y.:  *$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ /expanded graphite composite as form-stable phase change materials for thermal energy storage*, J. Therm. Anal. Calorim. 2013, 115, pp. 111-117.
- [44] Xu B., Li Z.: *Paraffin/diatomite composite phase change material incorporated cement-based composite for thermal energy storage*. Appl. Energy 2013, 105, pp. 229-237.
- [45] Lasfargues M., Bell A., Ding Y.: *In Situ production of titanium dioxide nanoparticles in molten salt phase for thermal energy storage and heat-transfer fluid applications*, J. Nanopart. Res. 2016, 18, pp. 1-11.
- [46] Tiagi V., Kaushik S.C.: *Development of phase change materials based microencapsulated technology for buildings: A review*. Renew. Sustain. Energy Rev. 2011, 15, pp. 1373-1391.
- [47] Huang J., Wang T., Zhu P., Xiao J.: *Preparation, characterization, and thermal properties of the microencapsulation of a hydrated salt as phase change energy storage materials*. Thermochim. Acta 2013, 557, pp. 1-6.
- [48] Korhammer K., Druske M.-M., Fopah-Lele A., Rammelberg H.U., Wegscheider N., Opel O., Osterland T., Ruck W.: *Sorption and thermal characterization of composite materials based on chlorides for thermal energy storage*, Appl. Energy 2016, 162, pp. 1462-1472.
- [49] Huang Z., Luo Z., Gao X., Fang X., Fang Y., Zhang Z.: *Investigations on the thermal stability, long-term reliability of  $\text{LiNO}_3/\text{KCl}$ –Expanded graphite composite as industrial waste heat storage material and its corrosion properties with metals*. Appl. Energy 2017, 188, pp. 521-528.
- [50] Cheng F., Wen R., Huang Z., Fang M., Liu Y.G., Wu X., Min X.: *Preparation and analysis of lightweight wall material with expanded graphite (EG)/paraffin composites for solar energy storage*, Appl. Therm. Eng. 2017, 120, pp. 107-114.
- [51] Xu T., Li Y., Chen J., Liu J.: *Preparation and thermal energy storage properties of lino 3-kcl-nano 3/expanded graphite composite phase change material*, Sol. Energy Mater. Sol. Cells 2017, 169, pp. 215-221.
- [52] Huang X., Alva G., Liu L., Fang G.: *Preparation, characterization and thermal properties of fatty acid eutectics/bentonite/expanded graphite composites as novel form-stable thermal energy storage materials*, Sol. Energy Mater. Sol. Cells 2017, 166, pp. 157-166.
- [53] Cui W., Zhang H., Xia Y., Zou Y., Xiang C., Chu H., Qiu S., Xu F., Sun L.: *Preparation and thermophysical properties of a novel form-stable  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ /sepiolite composite phase change material for latent heat storage*, J. Therm. Anal. Calorim. 2017, 20, pp. 1-7.