

# Phosphogypsum-Paraffin Composites for Low Temperature Thermal Energy Storage Applications <sup>†</sup>

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**Abstract:** Phosphogypsum (PG) is an environmentally hazardous industrial by-product of the fertilizer industry with an annual production of 300 Mt, with a utilization rate of only 15%. In this work, we propose a novel use-case for PG. The latter is combined with a commercial-grade paraffin to fabricate composite phase change materials (CPCMs), for thermal energy storage applications. CPCMs are fabricated following a comminution and sintering process. The fabricated materials exhibit a stable latent heat (75 J/g) after 96 cycles (25 to 100 °C), with a maximum average specific heat capacity of 1.54 J/gK at 60% paraffin content. The thermal conductivity is found to be 75% higher than pure paraffin, while the energy storage density is only 14% lower.

**Keywords:** phosphogypsum; paraffin; composite; material; thermal energy storage; waste valorization; industrial symbiosis



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## 1. Introduction

Currently, global energy production is dependent on non-sustainable pathways. This coupled with an ever increasing energy demand leads to considerable environmental challenges [1]. The solution to this involves the high penetration of renewables to the current energy production mix, with the sun being the most abundant source. However, one large barrier for solar energy is the infamous “duck curve” (demand–supply mismatch). This necessitates a certain degree of energy storage, which leads to a high number of conversion steps throughout the energy supply chain [2]. A higher number of conversion steps translates to higher inefficiency, which results in larger energy losses the majority of which are in the form of heat. Furthermore, a transition to a renewable-based life increases energy conversion steps, which further burdens the energy supply chain and necessitates a coordinated supply/demand optimization [2]. A higher number of conversion steps translates to higher energy losses due to efficiency issues, the majority of which are in the form of heat [3]. To combat this, the EU has set a 2030 target of 32.5% efficiency for energy consumption. This requires a further increase of 12.5% from 2020 levels [4]. One of the most promising cost-effective technologies that can provide leverage to this problem is thermal energy storage (TES) [3].

Latent heat TES (LHTES) systems are a promising sub-category of TES systems. They have considerably higher energy density than sensible ones and lower costs than thermochemical. Industrial deployments have been reported for peak-shaving of electricity grids, solar energy utilization and waste heat recovery [5].

The core principle of LHTES systems is centered on the ability of a material, commonly referred to as the phase change material (PCM), to absorb/release heat isothermally through

its transition from one state to another [6]. However, PCMs have several disadvantages, most notably, poor thermal conductivity, high volume expansion, corrosion and subcooling, which affect their performance but can be largely resolved by encompassing them in a porous matrix [7]. The resulting materials are called composite phase change materials (CPCMs).

Phosphogypsum (PG) is an industrial waste of the phosphate industry [8]. Typically, 4–6 tons of PG are produced per ton of phosphorous fertilizer [8]. Presently, annual PG production is estimated to be between 100–280 Mt [8]. The majority of the produced PG is either directly dumped in water bodies or stockpiled in within a confined lined or unlined disposal area, with an estimated management cost of 0.9 \$/ton [9]. This practice is highly problematic and potentially hazardous due to the acidic nature of PG as well as the traces of heavy metals and other impurities (i.e., fluorine) present in its structure [10]. Presently, only 15% of the produced PG is utilized [11], mostly in civil engineering applications as a construction and road embankment material and in agricultural applications as a soil improver [10].

Independent of origin, PG consists primarily of gypsum, which demonstrates good thermal stability, has a high surface area, and particle density. These properties make PG an ideal candidate as a supporting material for PCMs. In fact, gypsum based low-cost PCMs have been extensively investigated and applied in building envelopes for thermal management applications [12]. Commercial products, such as the MICRONAL from BASF are available. However, the use of PG as a supporting material for CPCMs and its use in TES industrial applications has been overlooked. To this end, in this work, we propose a novel valorization pathway for PG as an energy storage material and in this context, present a study on its use as a matrix material for paraffin targeting low-temperature waste heat/storage applications.

## 2. Materials and Methods

RT90, a commercial-grade paraffin, is the PCM used in this work, obtained from Rubitherm Technologies GmbH. The supporting matrix material is the PG obtained from the plant of Elfe SA Industry located in Kavala, Greece (Table 1). The PG is first heated to 450 °C for 15 h, to remove the majority of H<sub>2</sub>O (~34 wt.%) and facilitate the transition to anhydrite II (432 °C) [13], which demonstrates increased density and hardness, properties beneficial to the application. The CPCMs are then fabricated following a comminution process, where the PG and paraffin are mixed, milled and mixed again, followed by cold compression which involves the shaping of the milled powder mixture in a 15 mm diameter pellet using a compression load of 30 MPa. The pellet is then heated up to 110 °C (5 °C/min) followed by rapid cooling. PG-paraffin pellets are fabricated at 40–60 and 50–50 wt.% mass ratios.

**Table 1.** Chemical composition of the phosphogypsum obtained from “Elfe SA Industry”.

Element	SO <sub>3</sub>	CaO	H <sub>2</sub> O	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	NO <sub>3</sub> <sup>−</sup>	Cl <sup>−</sup>
Percentage (%)	46.31	33.52	17.38	0.86	0.51	0.23	0.06	0.04	0.2

X-ray Diffraction (XRD) measurements are conducted on a Bruker D8 Advance apparatus using a 2°/min step at room temperature (air atmosphere). Differential Scanning Calorimetry (DSC) measurements are conducted on a DSC3 Mettler Toledo apparatus. Measurements are done in air atmosphere with a heating rate of 5 °C/min according to the standards DIN51007 and following the sapphire method. Laser Flash Technique (LFA) is used to measure the thermal diffusivity of the materials on an LFA 427 apparatus (Netzsch). All samples are graphite coated with a graphite layer. The density of the samples is assessed using a helium pycnometer (Accupyc II 1340, Micromeritics).

Measurements are conducted after 96 cycles. Each cycle consists of a heating stage from 25 to 110 °C (5 °C/min), followed by a temperature plateau at 110 °C for 20 min and subsequent cooling to 25 °C (5 °C/min).

### 3. Discussion

#### 3.1. Density and Porosity

The porosity and density of the PG and CPCMs is assessed. The grain density of PG is found to be  $2.71 \pm 0.05 \text{ g/cm}^{-3}$ . Bulk density of the CPCMs is obtained through mass-volume measurements. The porosity is then derived using the density ratio formula.

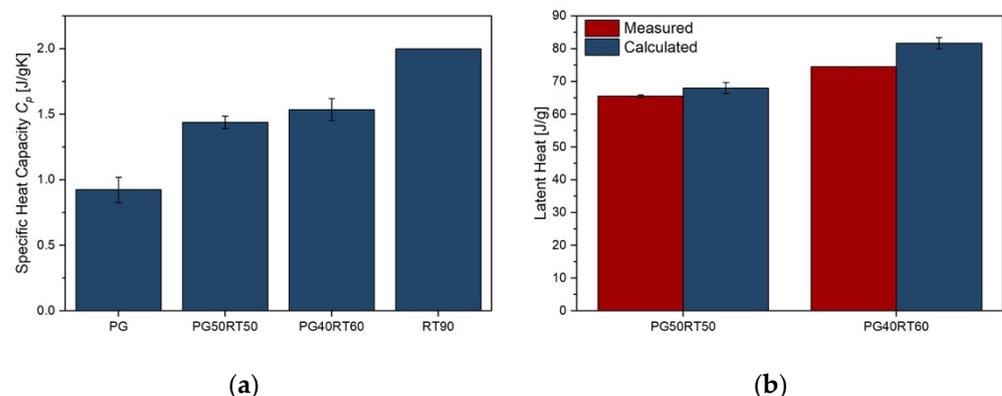
The density and porosity of PG remain almost constant throughout the cycling process (Table 2). A slight reduction in density is attributed to minor quantities of water that were not evaporated during the material preparation. CPCMs maintain a stable density. However, in the PG50RT50 case, the porosity of the sample increases. This is attributed to the thermal expansion and compressive strength of the latter.

**Table 2.** Left: CPCMs density versus number of cycles. Right: CPCMs porosity versus number of cycles.

No. of Cycles [-]	0	96	0	96
Property	Density [ $\text{g/cm}^3$ ]		Porosity	
PG	1.76	1.63	27.10	37.38
PG50RT50	1.28	1.15	27.97	34.96
PG40RT60	1.24	1.26	23.03	22.47

#### 3.2. Latent Heat and Specific Heat Capacity

The latent heat of the CPCM is measured after 96 cycles (Figure 1b). It is found to be in proximity to the theoretical values, which are derived from the expected in each case PCM (RT90) content and the latent heat values provided for RT90 by the manufacturer. This suggests good chemical compatibility between the paraffin and the PG, which is anticipated since previous studies have reported similar results for paraffin and gypsum, the latter being the primary constituent of PG.



**Figure 1.** (a) Average specific heat capacity of PG, CPCMs and RT90 in the temperature range of 25–100 °C after 96 cycles. (b) Measured and calculated latent heat of CPCMs.

The minor deviation, in latent heat, from theoretical calculations is typically associated with PCM leakage. To this end, the latent heat of the CPCM is measured after the 1st and 96th cycles. The value of the 1st cycle is found to be in closer proximity to the theoretical value. This indicates that most of the PCM leakage occurs in the first heating cycle with minor leakage in the subsequent 24 cycles, after which microstructural stability is achieved.

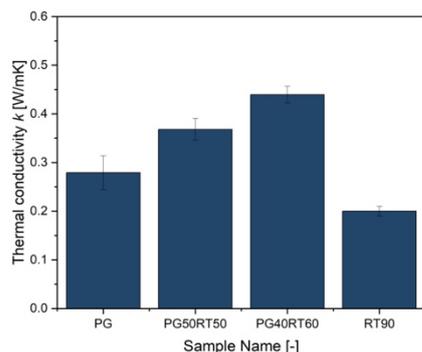
Similarly in the work of Karaipekli et al. [14] on gypsum/(C18-C24) mixtures, the latent heat was found to be 2.5% lower than that of the PCM. In their case, this was attributed entirely to PCM leakage from the gypsum matrix. Jeong et al. [15] measured the latent heat of CPCMs consisting of a blend of paraffins and gypsum and found it to be 3.4% lower at 20 wt.% and 30.5% lower at 30 wt.% PCM content. In the latter case, PCM leakage probably occurred.

Specific heat capacity ( $C_p$ ) defines the sensible storage capacity of the CPCM.  $C_p$  is measured in the operating temperature range (25–100 °C). However, due to the high error of the DSC measurement during phase transition, the  $C_p$  values for CPCMs above 75 °C are derived using mixing theory and the  $C_p$  values of the PG and those provided by the manufacturer for RT90.

Naturally, the RT90 has a higher  $C_p$  than the PG (Figure 1a). In terms of mixtures, as anticipated, the 0.4–0.6 PG-RT90 mass ratio demonstrates the highest average value: 1.54 J/g °C. In terms of temperature, the evolution of  $C_p$  is found to demonstrate a linear profile in all cases.

### 3.3. Thermal Conductivity

The thermal conductivity is calculated using thermal diffusivity measurements and the density and specific heat capacity values presented above. The benefit of encompassing paraffin in a PG matrix is apparent (Figure 2). The thermal conductivity of RT90 is 0.2 W/mK. That of PG is considerably higher (32.6%). Furthermore, the thermal conductivity of a CPCM is highly dependent on porosity. This is due to the low thermal conductivity of the air in voids, which results in a lower thermal conductivity than a bulk liquid/solid material. Since the porosity is improved by adding PCM (Section 3.1), the resulting thermal conductivity is highest when PG and RT90 are mixed (Figure 2). 60 wt.% RT90 demonstrates the lowest porosity and thus, the highest thermal conductivity. Concerning temperature evolution, CPCMs samples demonstrate an anticipated declining trend. For pure PG, the value remains constant within the statistical error.

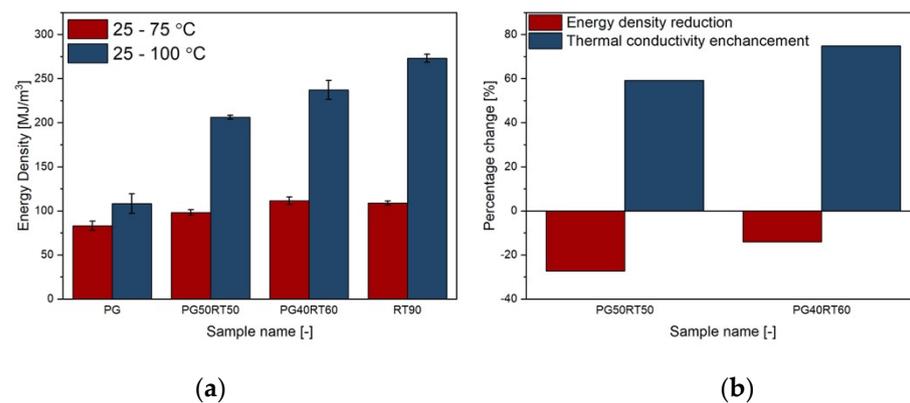


**Figure 2.** Average thermal conductivity of CPCMs and PG versus temperature after 96 cycles from 25 to 100 °C.

Kuzmanovic et al. reported the thermal conductivity of gypsum to be 0.35 W/mK, slightly higher than the one reported here for PG. Of course, as with PG, the properties of gypsum are also dependent on the raw material origin and processing methods. The addition of n-octadecane leads to an increase in thermal conductivity. As for RT90, the thermal conductivity of n-octadecane is substantially lower than that of gypsum.

### 3.4. Energy Storage Density

In the 25–75 °C range, PG demonstrates the lowest energy density and PG50RT90 the highest (Figure 3). This is anticipated as the heat storage capacity of pure PG is substantially lower than the RT90 and thus also the CPCMs. However, at this temperature range, the energy density is in the form of sensible heat. It is thus dependent, aside from the specific heat capacity, on the density of the material. Therefore, the low density of the paraffin counterplays its high specific heat capacity resulting in a low energy density, closer in magnitude to pure PG. At 25 to 100 °C, where the latent heat is taken into account, the paraffin outshines in performance.



**Figure 3.** (a) Energy storage density at 25–75 °C and 25–100 °C; (b) Energy density reduction compared with thermal conductivity enhancement.

Overall, substituting PG with paraffin results in a reduction of up to 40% in PCM content with only 14.3% losses in energy density. This aspect strongly underlines the benefit of using a waste material, such as PG for TES applications. On the other hand, the thermal conductivity is increased by up to 74.3%. Thermal conductivity is a critical parameter for charging and discharging any TES unit, particularly in waste heat recovery applications at an industrial level, where the availability of waste heat is in short time frames.

Utilization of PG provides, aside from apparent environmental benefits, a reduction associated with cost incentives. Transportation and storage of PG has been estimated to be up to 1% of the production cost of phosphoric acid [9]. Thus, substituting the content of RT90 with PG, indirectly, further reduces the overall material cost as the maintenance costs for PG are mitigated.

#### 4. Conclusions

Phosphogypsum (PG) is a by-product of the phosphoric fertilizer industry. Its management and disposal are highly problematic due to its traces of heavy metals and other hazardous impurities. Despite efforts, only 15% of that is utilized.

This work aims at defining a technically and economically feasible solution for the utilization of PG. It involves its transformation into an energy commodity and its potential utilization in a waste heat recovery/thermal management unit. To this end the PG is used as a carrier material for CPCMs consisting of PG and RT90 (a commercial paraffin). The main outcomes are the following:

- All fabricated CPCMs are found to be chemically stable after 96 cycles at 25–100 °C, as verified through stable latent heat.
- The density of the CPCMs is higher than the pure paraffin. Furthermore, the porosity of the fabricated CPCMs is lower than pure PG.
- The optimal specific heat capacity of CPCMs is found to be 1.55 J/gK at 60% paraffin content.
- PG40RT60 samples demonstrate the highest thermal conductivity, 0.46 W/mK on average in the examined temperature range.
- The energy storage density of PG40RT60 is 237.44 MJ/m<sup>3</sup>, only 14.03% lower than the pure paraffin (273.32 MJ/m<sup>3</sup>). This is due to the high particle density of PG.

To summarize, a novel energy commodity is presented that can be utilized in low temperature thermal management/waste heat recovery applications promoting a novel tangible case of industrial symbiosis.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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