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1. Introduction

Decarbonisation processes and the penetration of renewable energy sources are reducing the share of conventional energy sources in the national energy mix [1]. This reduces the predictability of energy generation and, as a result, leads to potential problems in maintaining the stability of the electricity grid [2]. The main challenge for the grid operator is to increase the flexibility of existing energy sources. Renewable energy sources, which are dependent on current weather conditions, can buffer the energy produced, for example by storing heat [3]. Thermal integration of energy systems appears to be a key aspect in improving the conditions for power generation. Thermal integration makes it possible to store electricity in the form of heat for many hours and use it when electricity demand increases.

There are several types of heat management processes in energy systems:

- Heat storage in the energy system loop - Heat storage is at the heart of system operation - for example in an adiabatic compressed air energy storage system (A-CAES) [4]. In the case of this system, heat storage is a key component that eliminates the need to combust natural gas during the energy storage discharge phase. The heat storage unit accumulates the heat from gas compression during the charging stage and stores it during the storage stage.
- Heat storage as an integrator of system components - Heat storage enables increased flexibility of the energy system. Kosman et al [5,6] presented a concept for the construction of a heat storage tank within a conventional coal-fired power plant. The basis of their work was the desire to maintain constant operation of a coal-fired boiler in the face of variable and unpredictable electricity demand from the consumer. Keeping the boiler parameters constant has a positive effect on its efficiency and technical condition. The energy accumulator in such a system acts as an integrator between the power boiler and the steam generator upstream of the steam turbine. The hot fluid that has removed heat from the boiler is directed to a hot tank. When there is an increased demand for electricity, the hot fluid is directed to the steam generator, which in turn is directed to the turbine that drives the generator. This solution ensures that electricity production can be adjusted to meet consumer demand. Similar concepts have been presented for the implementation of Generation III and Generation IV nuclear reactors [7,8].

Due to the nature of heat storage processes, it is necessary to define the materials that can store energy. Depending on the role to be played by heat storage, the potential materials may have different suitability ratings based on their characteristic parameters.

2. Goal of the work

The aim of this study in the range of task *T.5.1. Experimental study of heat storage materials and Thermal Energy Storage tank* (WP5. Heat storage in post-mining infrastructure) in HESS project is to define the key thermophysical, mechanical, chemical and economic parameters of accumulator materials that are indicated as potential heat accumulators. Depending on the intended use and the method of heat storage and transfer within the system, different storage materials will be preferred. The *Hybrid energy storage system using post-mining infrastructure* (HESS) project involves the analysis of a multi-variant energy storage system in which heat will play both a key role within the system cycle and a supporting role to maintain and stabilise electricity production.

The research part of the study is divided into two groups:

- Experimental - Tests were conducted within this group to demonstrate the suitability of the ceramic material for heat storage. For this purpose, the NETZSCH STA 449 F3 Jupiter analyser was employed, which enables simultaneous TG-DSC measurements [9]. The measurement allows for the determination of the change in mass of the sample under the influence of temperature increase, which directly enables the identification of the physicochemical transformation of the material under the influence of temperature. This is a crucial factor in determining the suitability of a material for use in heat storage tanks. The storage material must demonstrate consistent performance over numerous cycles under varying temperature loads. The ceramic material was Alferrock, produced from red mud [10], a byproduct of the bauxite industry. The declared chemical composition of the samples is as follows: hematite (Fe_2O_3), corundum (Al_2O_3), rutile (TiO_2) and/or anatase (TiO_2), quartz (SiO_2), and so forth. Additionally, perovskite (CaTiO_3) and, if optionally, pseudobrookite ($(\text{Fe}^{3+}, \text{Fe}^{2+})_2(\text{Ti}, \text{Fe}^{3+})\text{O}_5$) and/or nepheline ($(\text{Na}, \text{K})[\text{AlSiO}_4]$) may be present. This material has already been proposed as an admixture for solar salt, which has been investigated in a solar energy storage system [11]. The material was also investigated using a TCi analyser with an MTPS sensor, which allows the determination of the material's thermal conductivity.
- Literature – a comprehensive literature review was conducted within the context of the literature group, with a particular focus on materials proposed as heat storage materials. The identification was conducted in three principal categories. (a) Solid materials for sensible heat storage; (b) Liquids for sensible heat storage; (c) Phase change materials for sensible and latent heat storage. The division adopted makes it possible to determine the preferred storage materials for both heat storage within the main system component and thermal integration of the components. A key aspect was the definition of three reference temperature levels: 100°C, 300°C and 500°C. These temperatures correspond to processes with different temperature potentials implemented within energy storage and generation systems.

The assessment was conducted in four principal categories. (a) Thermal properties; (b) Physical properties; (c) Chemical properties; (d) Economic factors. The analysis led to the selection of one material from each of the defined groups (solids, liquids, PCMs) proposed for heat storage at predefined heat temperature levels (100 °C, 300 °C, 500 °C). This resulted in the identification of nine proposed materials, which were subsequently evaluated in each category. These materials will be subjected to further experimental and numerical analyses as part of the implementation of the HESS project. It should be noted that the selected materials

represent a compromise between favourable thermophysical parameters and unit price and availability. The evaluation of solid materials used for sensible heat storage was conducted according to the following criteria:

Table 1. Evaluation parameters for solid materials

Properties	Desirable parameter
Thermal properties	Temperature range suitable for desired operation High specific heat C_p Thermal conductivity
Physical properties	Density Mechanical strength
Economic factors	Low-cost Available in large quantities

The fluids employed for the storage of sensible heat were evaluated in accordance with the following criteria:

Table 2. Evaluation parameters for liquids

Properties	Desirable parameter
Thermal properties	Temperature range suitable for desired operation Specific heat C_p Thermal conductivity
Physical properties	Density Viscosity
Chemical properties	High chemical stability (no decomposition) Low corrosive Non-toxic Non-flammable and non-explosive
Economic factors	Low-cost Available in large quantities

The evaluation of phase-change materials for sensible and latent heat storage was conducted in accordance with the following criteria:

Table 3. Evaluation parameters for phase-change materials

Properties	Desirable parameter
Thermal properties	Temperature range suitable for desired operation High heat of fusion

	High specific heat C_p High thermal conductivity
Physical properties	High density of PCM Low density change during phase change and thus a low volume change Minimal supercooling effect Low hygroscopicity and low viscosity
Chemical properties	High chemical stability (no decomposition) Low corrosive Non-toxic Non-flammable and non-explosive
Economic factors	Low-cost Available in large quantities

The above criteria were defined as:

- Thermal properties – Temperature range suitable for desired operation – The category corresponds to three defined operating and heat storage temperature levels, viz: 100 °C, 300 °C, 500 °C. For solids and liquids, it was assumed that the maximum permissible temperature is the highest demonstrated operating temperature within the energy storage system or technical data published by the technology supplier. For phase-change materials, the operating temperature was taken as the storage loading temperature. It is higher than or equal to the melting point of the PCM mix. Is important to note that a PCM material can function as a liquid sensible heat accumulator after melting or as a solid heat accumulator before melting. Specific heat is a thermophysical parameter that determines the amount of heat that is required to be applied to a kilogram of heat storage material to raise its temperature by one degree. Thermal conductivity is a thermophysical parameter that determines the ability of a material to conduct heat within it during heat exchange or storage. In order to define the required parameters of the accumulation material in each case, it is necessary to take into account the characteristics of the specific heat exchanger or heat store. What is important is the operating cycle of the heat store, the way it is charged and discharged, and the expected range of temperatures to be achieved.
- Physical properties - the density of the material is a characteristic parameter that is one of the factors influencing the required volume of the heat storage tank. Mechanical strength is determined for solid storage materials. It is an important parameter from the perspective of heat storage in packed beds, in which the lower layers of the heat storage tank are subjected to the greatest stress.
- Chemical properties - the chemical properties of the accumulation materials were evaluated in terms of their toxicity, corrosivity, propensity to ignite, chemical stability under high temperatures and long-term cyclic operation.
- Economic factors – a consideration of all factors influencing the accessibility and financial implications of procuring accumulation material, with an emphasis on the unit price of the material itself. The price of phase-change material is a component of the price of a single pellet and, consequently, of a PCM bed. The greater corrosivity of the PCM material increases the material requirements of the PCM pellet housing itself and

thus the price. Another economic aspect is the significant differences in the melting heat of phase-change materials, in extreme cases this can mean the use of two or three times the amount of the material itself to achieve an identical heat capacity of the magnesium.

High melting point PCMs consist mainly of mixtures of inorganic salts. The properties of the individual salts affect the properties of the resulting PCM. As shown in Table 4, salts possess both advantages and disadvantages. For example, fluoride and chloride salts are corrosive, and fluorides are also highly toxic [12]. On the other hand, chlorides are a potential substitute for nitrates. Chloride salts are abundant, inexpensive, and have good thermal stability [13].

Table 4. Basic characteristics of salts with an identification of their advantages and disadvantages

Salts mixtures of	Advantages	Disadvantages
Fluorides	High latent heat	Highly toxic and corrosive, high melting temperature, expensive (especially LiF)
Chlorides	Usually non-toxic (MgCl_2 , NaCl , KCl), low price, good availability, wide operating temperature range	Highly corrosive, very hygroscopic (MgCl_2), higher price of anhydrous salts than hydrated salts, which are more available (e.g., MgCl_2 , MnCl_2)
Nitrates	Low price, good availability, low-toxicity, low corrosivity	Thermal stability ($<500\text{ }^\circ\text{C}$).
Hydroxides	Usually lower the melting point of salts mixtures, low price, good availability	Highly corrosive and very caustic, high hygroscopicity (NaOH , LiOH , KOH)
Carbonates	Usually non-toxic (K_2CO_3 , Na_2CO_3 , LiCO_3), non-expensive (excluding Li salts), high thermal stability	High melting temperature (usually $>400\text{ }^\circ\text{C}$)
Lithium salts	High latent heat, (LiOH-LiF $>500\text{ kJ/kg}$), medium toxicity (excluding LiF)	Expensive, high hygroscopicity (LiF , LiCl , LiNO_3)

3. Results analysis

3.1 Experimental analysis

The Alferrock ceramic material was tested in the form of spherical elements with a diameter of approximately 16 mm. Figure 1 and Figure 2 show the particles under test.



Fig. 1 Copper-coloured Alferrock material sample - Case A



Fig. 2 Grey-coloured Alferrock material sample - Case B

The material exhibited different colours, namely copper or grey, depending on the concentrations of the individual compounds. The structure of the material was tailored to the specific requirements of the study. Figure 1 shows the results of the thermogravimetric/differential scanning calorimetry (TG/DSC) analysis of the copper-coloured sample. Figure 2 shows the results of the TG/DSC analysis of a sample with a grey colour. During the course of the testing procedure, the samples were subjected to a heating process, the temperature of which was increased to approximately 1030°C at a rate of 50°C per minute.

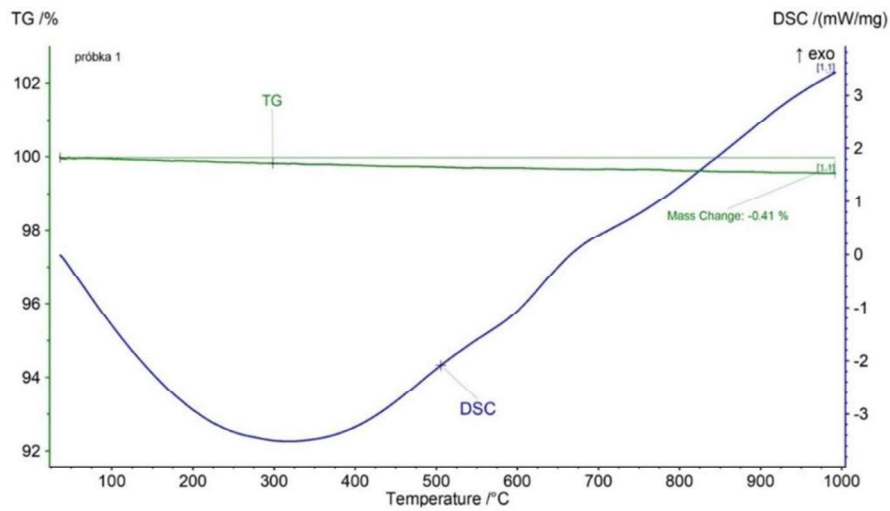


Fig. 3 Variation of the sample mass depending on its temperature during the test – case A

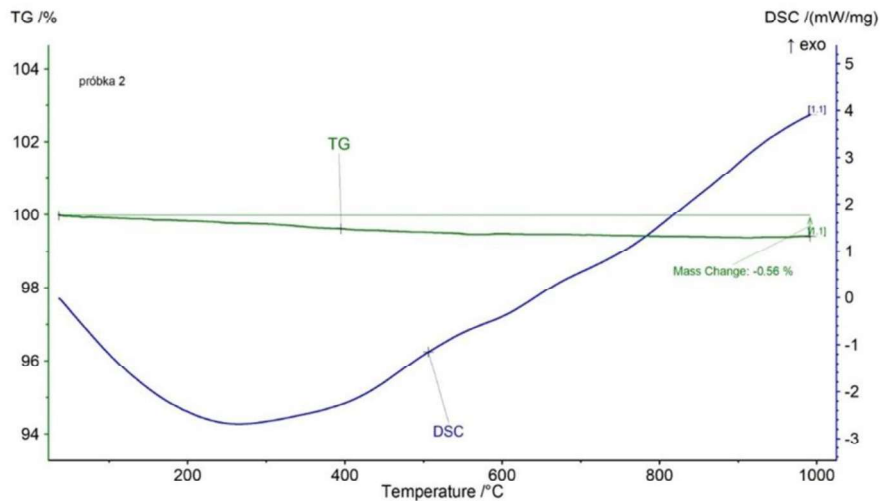


Fig. 4 Variation of the sample mass depending on its temperature during the test – case B

The results presented in Figures 3 and 4 indicate a slight loss of mass in the samples subjected to significant heating of the accumulation material. It was observed that the copper-coloured sample (Figure 3, case A) exhibited a loss of 0.41% of its initial mass, while the grey-coloured sample (Figure 4, case B) demonstrated a loss of 0.56%. Figure 5 presents the results of the thermogravimetric analysis and differential scanning calorimetry during the cyclic heating and cooling of the copper-coloured sample. Figure 6 presents the results of the TGA and DSC during the cyclic heating and cooling of the grey-coloured sample.

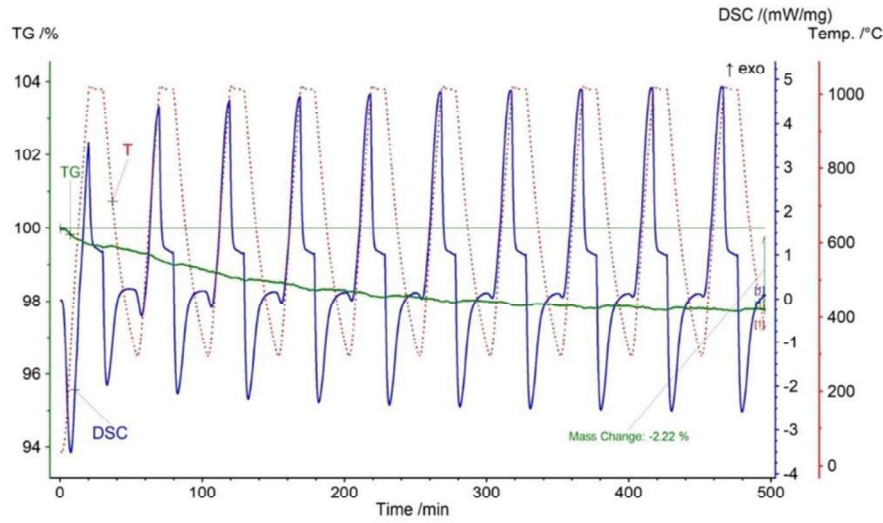


Fig. 5 Change in sample mass during cyclic heating and cooling – case A

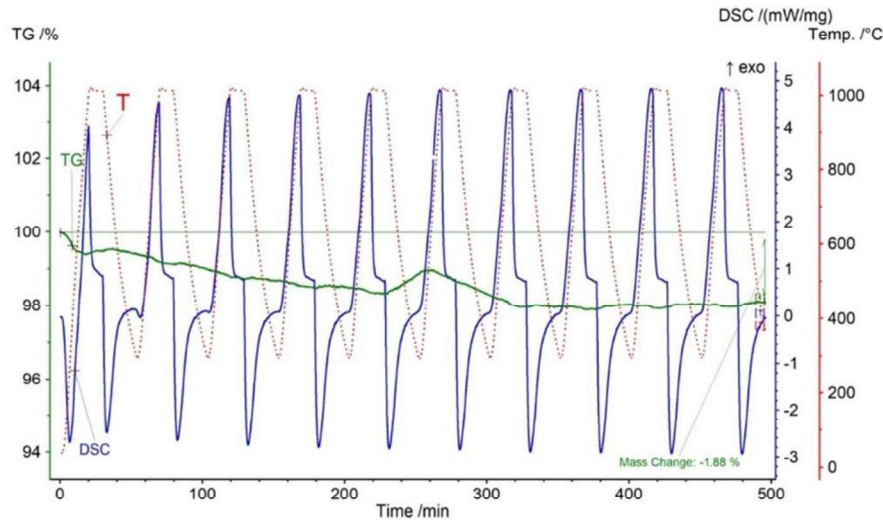


Fig. 6 Change in sample mass during cyclic heating and cooling – case B

The samples were subjected to heating between 40°C and 1030°C at a rate of 50°C per minute, with a 10-minute stagnation period at each case. Cooling was conducted to 300°C at the same rate. A total of 10 cycles were completed, comprising heating, temperature stagnation, and cooling of the sample. The results demonstrated that the weight loss of the test material was 2.22% for the copper-coloured material (Figure 1, case A) and 1.88% for the grey-coloured material (Figure 2, case B), respectively.

The objective of the tests conducted using TCi was to measure the thermal conductivity of the samples. The results indicated that the average value of this parameter for the Alferrock ceramic material was 0.12 W/mK. The tests were conducted at an average ambient temperature of 20.94°C. Prior research has demonstrated that the heat capacity of this material is 791 J/kgK at 30°C and 1037 J/kgK at 584°C. Additionally, the density of the material exhibits a range of 3630 kg/m³ to 3930 kg/m³ at 1000°C [14].

3.2 Literature analysis of storage materials

3.2.1 Solid materials for sensible heat storage

A summary of the fourteen solid materials that were identified in the research as potential heat storage materials is presented in Table 5. In all cases, the heat storage process occurred within a porous bed, where the heat flux was transferred directly between the fluid and the solid material. It is important to note that the porous bed heat storage design must consider the porosity value, which typically falls within the range of 0.36-0.40. The porosity of the rock bed directly affects the final volume of the heat storage, as it accounts for the bulk volume of the bulk material. The data presented were derived from an average of analyses of literature sources.

Table 5. Summary of the characteristic parameters of solid materials [15–36]

Type of rock/ Parameter	Density, kg/m ³	Specific Heat, J/kgK	Volumetric thermal capacity, kJ/m ³ K	Thermal conductivity, W/mK
Basalt	2768.0	852.1	2358.6	2.1
Granite	2642.8	859.7	2272.1	3.0
Rholite (25°C)	2677.7	865.3	2317.0	2.0
Gneis (25°C)	2777.5	876.0	2433.2	3.0
Sandstone	2481.5	774.5	1921.9	2.7
Limestone	2600.0	810.0	2106.0	2.2
Quartzite	2576.0	818.3	2107.8	5.2
Halite	2170.0	882.5	1915.0	6.1
Magnetite (100°C)	4890.0	745.0	3643.1	5.6
Cofalit	3120.0	1034.0	3226.1	2.1
Castable ceramics	3500.0	866.0	3031.0	1.4
Concrete	2383.3	916.0	2183.1	1.0
Sinter bed (25°C)	3603.8	606.7	2186.3	-
Alumina	3984	758.64	3022.4	33.38

The data presented were obtained for an ambient temperature of 20°C. In the absence of relevant data for this temperature, the corresponding reference temperature is shown in brackets. The defined materials are, by far, dominated by those of natural origin. Common rocks such as granite and basalt are characterised by relatively similar values of thermophysical parameters. Magnetite has the highest density value, but at the same time has the lowest heat capacity value. The bulk heat capacity demonstrates that magnetite exhibits the most favourable parameters (3643 kJ/m³K). It is important to note that the thermophysical parameters of the solid materials presented are temperature-dependent. Figure 7 illustrates the temperature dependence of the heat capacity of selected materials, while Figure 8 depicts the temperature dependence of the thermal conductivity of selected materials.

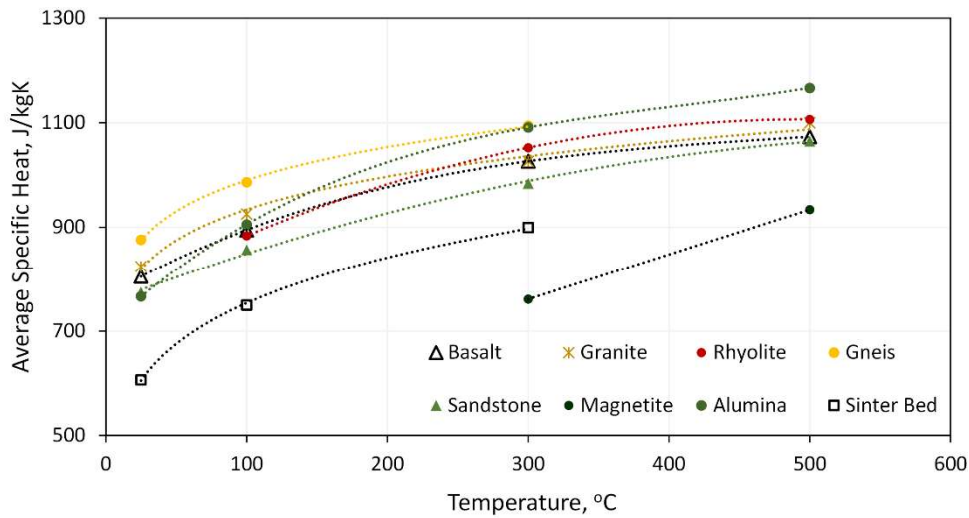


Fig. 7 Temperature dependence of heat capacity of selected solid materials

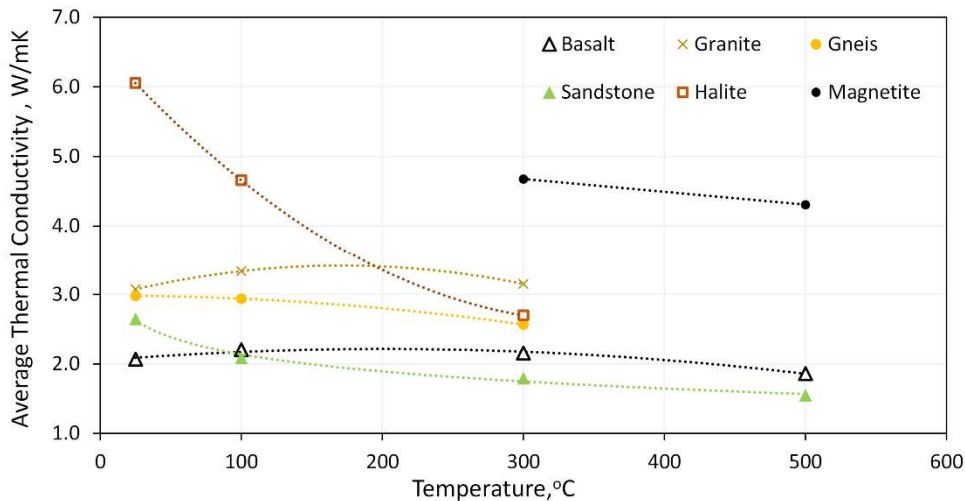


Fig. 8 Temperature dependence of the thermal conductivity of selected solid materials

In the case of all materials for which correlations were defined on the basis of temperature-dependent thermophysical parameters, it was established that the value of heat capacity increases in line with rising temperatures. The lowest heat capacity value was observed in magnetite. Rock materials such as gneiss, granite and basalt exhibited similar heat capacity values. With regard to the thermal conductivity coefficient, a decrease in this parameter was recorded with an increase in temperature. It is noteworthy that, according to Table 5, alumina has the highest thermal conductivity value among the classified solid materials.

Figure 9, derived from a comprehensive literature review, illustrates the range of values for the thermophysical parameters of basalt.

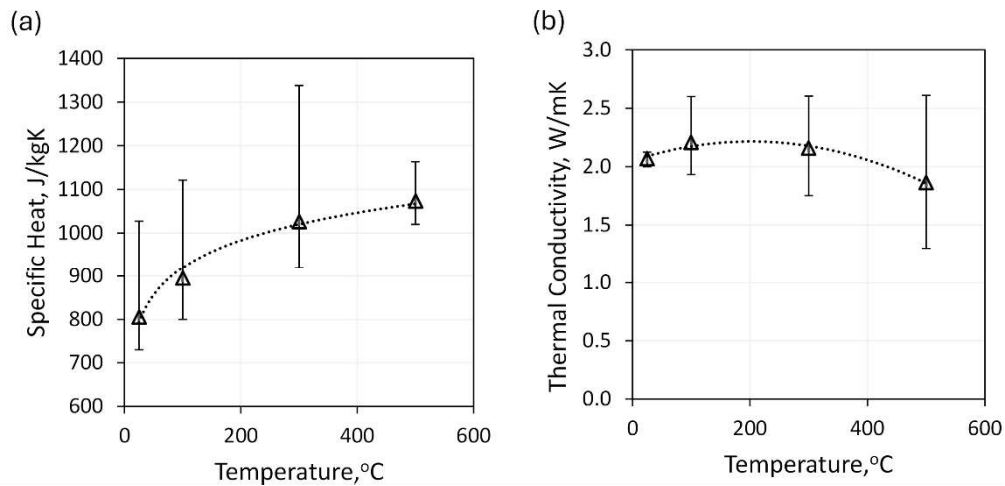


Fig. 9 The temperature-dependent range of basalt parameters: (a) heat capacity; (b) thermal conductivity coefficient.

The data presented in Figures 9(a) and 9(b) demonstrate that the thermophysical properties of natural materials exhibit a significant dependence on the source of the samples under examination. It is possible that discrepancies in values may reach as high as 25%. In their study, Nahhas et al. [18] analysed the discrepancies between the thermophysical parameters of basalt when cycled up to a temperature of 700°C. The study demonstrated that basalt from France and Egypt exhibited disparate fracture levels, contingent on the mining region. Similarly, comparable relationships are observed in the compressive strength of the materials. The preferred methods for determining this value are not aligned with the form of the heat accumulator materials. The mean compressive strength value for basalt was recorded at 29.79 N/mm², while granite exhibited a mean value of 27.89 N/mm². Consequently, the precise determination of the properties of a potential heat storage tank will be subject to a relatively high degree of uncertainty due to the lack of precise data. For design work, it will be necessary to investigate locally available or desirable rock materials in order to adequately estimate the required volume of storage material.

Table 6 presents the cost of selected materials.

Table 6. Cost of solid materials [20,33,37,38]

Type of solid material	Cost, €/kg
Basalt	0.11
Magnetite	0.46
Quartzite	0.04
Limestone	0.03–0.32
Concrete	0.03-0.08
Alumina	1.62
Cofalit	1.2
Cermic	4.5-9

The data presented in Table 6 indicate that natural materials (e.g. basalt, limestone) are characterised by a relatively low price, which is also a consequence of their extensive

availability. In contrast, ceramic materials are characterised by a higher price, due to the fact that they can be moulded into shapes defined by the client.

The maximum operating temperatures defined from the literature review for solid materials are as follows: (a) ceramic – 1000 °C; (b) basalt – 700 °C; (c) sandstone – 600 °C; (d) rholite – 550 °C; (e) quartzite – 550 °C; (f) halite – 300 °C. These temperatures refer to scientific studies in which the material in question has been used as a potential heat accumulator. It should be noted that these are not the maximum possible operating temperatures for these materials. As the operating temperature increases, the structural requirements of other components also increase, which increases the potential cost of the system. For halite, studies have been conducted on the thermophysical parameters for temperatures higher than 300 °C [39].

3.2.2 Sensible heat storage fluids

The table presents six materials that are defined within the category of fluids dedicated to sensible heat storage processes.

Table 7. Summary of the characteristic parameters of liquids [33,38,40–46]

Composition	Substance	$t_{\min}, ^\circ\text{C}$	$t_{\max}, ^\circ\text{C}$	Density, kg/m^3	Specific Heat, J/kgK	Thermal Conductivity, W/mK	Viscosity, mPas
$\text{NaNO}_3\text{--KNO}_3\text{--NaNO}_2$	HITEC	142	530-535	1637-1640	1560-1562	0.382	2.6
$\text{NaNO}_3\text{--KNO}_3\text{--Ca(NO}_3)_2$	HITEC XL	130	480-550	1959-1960	1430-1432	0.519	4.19
$\text{NaNO}_3\text{--KNO}_3$	Solar salt	260	600	1817-1820	1517-1520	0.519-0.525	1.57
	Therminol 66	-9	343	909-910	2070-2072	0.109	1.2
	Therminol VP-1	12	400	909	2066	0.113	0.37
	Rapeseed oil	7	250	843	2383	0.195	7.59

The liquids presented in Table 7 are characterised by a relatively wide range of applicability, although this is smaller than for solid materials. Solar salt exhibits the highest recorded operating temperature, with a range of 260 to 600 degrees Celsius. This enables it to meet the conditions for two defined temperature levels: 300 and 500 degrees Celsius. Additionally, this fluid exhibits the highest heat transfer coefficient value, estimated at approximately 0.522 W/mK. Of the fluids presented, only rapeseed oil is unable to function at the two defined temperature levels and must be limited to the 100 °C level. Thermal oils (Therminol 66 and Therminol VP-1) have the requisite thermophysical parameters, which favours their use in systems with heat storage. However, they are more toxic than other fluids. Table 8 provides an estimated cost for the defined fluids.

Table 8. Cost of liquids [33,38,40–46]

Composition	Substance	Cost, €/kg
$\text{NaNO}_3\text{--KNO}_3\text{--NaNO}_2$	HITEC	0.86
$\text{NaNO}_3\text{--KNO}_3\text{--Ca(NO}_3)_2$	HITEC XL	1.33
$\text{NaNO}_3\text{--KNO}_3$	Solar salt	0.47
	Therminol 66	0.93
	Therminol VP-1	3.68
	Rapeseed oil	0.74

The data presented in Table 8 indicates that Solar Salt has the lowest unit price, which, when considered alongside its wide operating temperature range, makes it a favourable option for use as a heat storage material. The highest unit cost is observed in Therminol VP-1, which has a maximum operating temperature of 400 °C and is 56 °C higher than the maximum operating temperature of Therminol 66, which is almost four times cheaper.

3.2.3 Phase change materials for storing latent and sensible heat

Tables 9-11 shows mixtures of inorganic salts, used as PCMs, whose melting point is in the range of 100-500°C. The table shows both physical, thermal and chemical properties that were collected from the literature review (references are shown in the table). As can be concluded from Table 4, commercial mixed-salts are predominantly nitrate-based for valid reasons. Nitrate salt mixtures have a relatively low melting point (100-200°C), which makes them suitable for use as heat transfer fluids (HTF). The low melting point facilitates the use of latent heat for energy storage, as it is easier to reach a lower melting point. Nitrates possess low hygroscopicity, are relatively inexpensive, have low toxicity, and are not corrosive.

Table 9. Summary of the characteristic parameters of phase-change materials – Part A [47–59]

Composition, % wt.	Density, kg/m ³ (25°C)	Specific Heat, J/(kgK)	Thermal conductivity, W/mK (liquid)	Melting temperature, °C	Heat of fusion, J/g	Toxic hazard	Hygroscopicity
38 KNO ₃ - 15 NaNO ₃ - 47 LiNO ₃	-	1600	0.5	100	-	H, Ir	2
54 KNO ₃ - 20 NaNO ₃ - 26 LiNO ₃	-	1090	-	118	-	H, Ir	2
52 KNO ₃ - 18 NaNO ₃ - 30 LiNO ₃	1.975 (140°C), 1.78	1640	-	123	155	H, Ir	2
48 Ca(NO ₃) ₂ - 45 KNO ₃ - 7 NaNO ₃ (Hitec XL)	1.992 (300°C)	1272-1450	0.52 (300°C)	120, 130	55.4	H, Ir	2
66.6 KNO ₃ - 10 LiNO ₃ - 23 Ca (NO ₃) ₂	-	1500 (300°C)	0.5696	136	-	H, Ir	2
67 KNO ₃ -14 LiNO ₃ - 19 Ca (NO ₃) ₂ (HPHTE-A)	-	2080 (300°C)	0.506	137	-	H, Ir	2
65 KNO ₃ - 10 LiNO ₃ - 25 Ca (NO ₃) ₂ (HPHTE-C)	-	1400 (300°C)	0.5791	138	-	H, Ir	2
68.6 ZnCl ₂ -7.5 NaCl - 23.9 KCl	2 (300°C)	810	-	204	-	H, C	3
60 NaNO ₃ - 40 KNO ₃ (Solar Salt)	-	1600	0.55 (565°C)	220-223, 246	113-117	Ir	1
93.9 NaNO ₃ - 4.2 NaCl - 1.8 NaF	-	1760 (400°C)	-	288	211	T, Ir	1
32.1 Li ₂ CO ₃ - 34.5 K ₂ CO ₃ - 33.4 Na ₂ CO ₃ (LiNaK)	-	1400-1500, 1610	1.60 (l)-1.69 (s)	397, 378	273-276	H, Ir	2
54.2 K ₂ CO ₃ - 28.1 Na ₂ CO ₃ - 17.7 LiF	-	1900	1.17	421	227	T, Ir	3
NaCl - CaCl ₂ - MgCl ₂ (SYSU-C4)	-	830, 1190	-	424	190	Ir	2
62 K ₂ CO ₃ - 38 Li ₂ CO ₃	-	1600	-	488	-	H, Ir	2

Table 10. Summary of the characteristic parameters of phase-change materials – Part B [47–59]

Composition, % wt.	Density, kg/m ³ (25°C)	Specific Heat, J/(kgK)	Thermal conductivity, W/mK (liquid)	Melting temperature, °C	Heat of fusion, J/g	Toxic hazard	Hygroscopicity
60 KNO ₃ - 30 LiNO ₃ - 10 Ca(NO ₃) ₂	-	1395	-	132	-	H, Ir	2
67 KNO ₃ - 33 LiNO ₃	1.93 (140°C)	-	-	133	170	Ir,	2
61 NaOH - 39 NaNO ₂	-	2070 (291-300°C)	-	237	294	T, Ir	3
90.8 LiNO ₃ - 9.2 Ba(NO ₃) ₂	-	-	-	253	368	T, Ir	2
40.4 NaOH - 59.6 NaNO ₃	-	1920 (290-300°C)	-	266	278	C, Ir	3
85.8 NaOH - 7.8 NaCl - 6.4 Na ₂ CO ₃	2.13	2510	-	282	316	C	3
59.7 NaOH - 24.7 NaCl - 15.7 Na ₂ CO ₃	-	1.51 (450-600°C)	-	347	-	C, Ir	3
86.3 NaNO ₃ - 8.4 NaCl - 5.3 Na ₂ SO ₄	-	-	-	287	234	Ir	1
5 NaBr-25 KBr- 55 LiBr- 15CaBr ₂	-	-	-	313.2	-	H, Ir,	3
4.9 LiF - 47.8 LiCl - 47.2 LiVO ₃	-	-	-	340	177	T, Ir	3
56 KCl - 44 LiCl	-	-	-	348	170	H, Ir	3
22.9 KCl - 60.6 MnCl ₂ - 16.5 NaCl	-	-	-	350	215	T, Ir	2
71.8 KCl - 28.2 LiCl	-	-	-	353	266	H, Ir	3
68.2 MgCl ₂ - 14.0 NaCl - 17.8KCl	-	1000 (500–800°C)	-	380	-	0	3
55 MgCl ₂ - 24.5 NaCl - 20.5 KCl	-	1180 (455-600°C)	-	387	284	0	3
64 MgCl ₂ - 36 KCl	2.19	840-960, 1155	0.83	470, 473	388, 310	0	3
48.8 MnCl ₂ - 38.1 KCl - 13.1 NaCl	-	-	-	390	230	T, Ir	2
50 MgCl ₂ - 30 NaCl - 20 KCl	-	-	-	401	85-100	0	3
54.6 KCl - 45.4 MnCl ₂	-	-	-	416	210	T, Ir	2

Table 11. Summary of the characteristic parameters of phase-change materials – Part C [47–59]

Composition, % wt.	Density, kg/m ³ (25°C)	Specific Heat , J/(kgK)	Thermal conductivity, W/mK (liquid)	Melting temperature, °C	Heat of fusion, J/g	Toxic hazard	Hygroscopicity
64.3 MnCl ₂ - 35.7 NaCl	-	-	-	425	230	T, Ir	2
78.7 LiOH - 21.3 LiF	-	-	-	427	1163	T, Ir, C	3
59.6 KCl - 40.4 MgCl ₂	-	-	-	429	271	0	3
56.1 MgCl ₂ - 43.9 NaCl	-	-	-	430	320	0	2
54 KCl - 46 ZnCl ₂	2.41 (s)	670/880	0.83	432	218	H, C	2
75.8 MnCl ₂ - 24.2 KCl	-	-	-	450	237	T, Ir	2
52 MgCl ₂ - 48 NaCl	2.23	920/1000	0.95	450	430	0	3
29.2 LiF - 59.1 KF - 11.7 NaF	-	-	-	454	325-414	T, Ir	3
74.2 MnCl ₂ - 25.8 KCl	-	-	-	456	206	T, Ir	2
44.8 NaCl - 55.2 MgCl ₂	-	-	-	459	333	0	3
58.5 CaCl ₂ - 41.5 LiCl	-	-	-	475	270	H, Ir	3
63 LiF - 37 LiCl	-	-	-	485	403	T, Ir	3
57.8 KF - 42.2 LiCl	-	-	-	487	344	T, Ir	3
62 K ₂ CO ₃ - 38 Li ₂ CO ₃	1.967 (577°C)	1600	-	488	NA	H, Ir	2
72 CaCl ₂ - 1.5 CaF ₂ - 26.4 NaF	-	-	-	490	264	T, Ir	3
67 KF - 33 LiF	-	-	-	493	458	T, Ir	3
56 Na ₂ CO ₃ - 44 Li ₂ CO ₃	2.32	1800/2090	2.09	496	370	H, Ir	1
67 CaCl ₂ - 33 NaCl	2.16	840/1000	1.02	500	281	Ir	3

In Tables 9-11, the hygroscopicity of PCM was estimated based on the deliquescence point (DP) of the individual salts at 25°C, included in the PCM. The DP denotes the relative humidity level (RH, %) at which a salt absorbs moisture from the air. Below this RH level, the salt will begin to dry out. The DP depends on the type of salt and temperature. Moreover, the presence of other salts, such as chlorides, may also increase the hygroscopicity, which may lead to the PCM absorbing more water than the individual components.

Tables 9-11 presents a 0–3 scale for hygroscopicity, with 0 representing salts that are non-hygroscopic (relative humidity (RH) > 90%, e.g., KNO₃), 1 denoting salts of low hygroscopicity (RH 70–89%, e.g., NaCl), 2 representing salts of high hygroscopicity (RH 30–69%, e.g., MgCl₂), and 3 representing salts that deliquesce very easily even at low humidity (RH < 30%, e.g., NaOH). The data on potential health hazards were derived from the safety data sheets of the individual chemicals included in the PCM.

The estimated prices of PCM were based on the prices of the individual chemicals contained in the PCM.

Table 12. Cost of phase-change materials – Part A

Composition, % wt.	Price, €/kg
38 KNO ₃ - 15 NaNO ₃ - 47 LiNO ₃	17.90
54 KNO ₃ - 20 NaNO ₃ - 26 LiNO ₃	10.26
52 KNO ₃ - 18 NaNO ₃ - 30 LiNO ₃	11.72
48 Ca(NO ₃) ₂ - 45 KNO ₃ - 7 NaNO ₃ (Hitec XL)	0.57
66.6 KNO ₃ - 10 LiNO ₃ - 23 Ca (NO ₃) ₂	4.37
67 KNO ₃ -14 LiNO ₃ - 19 Ca (NO ₃) ₂ (HPHTF-A)	5.85
65 KNO ₃ - 10 LiNO ₃ - 25 Ca (NO ₃) ₂ (HPHTF-C)	4.36
68.6 ZnCl ₂ -7.5 NaCl - 23.9 KCl	0.61
60 NaNO ₃ - 40 KNO ₃ (Solar Salt),	0.69
93.9 NaNO ₃ - 4.2 NaCl - 1.8 NaF	0.55
32.1 Li ₂ CO ₃ - 34.5 K ₂ CO ₃ - 33.4 Na ₂ CO ₃ (LiNaK)	9.89
54.2 K ₂ CO ₃ - 28.1 Na ₂ CO ₃ - 17.7 LiF	5.40
NaCl - CaCl ₂ - MgCl ₂ (SYSU-C4)	-
62 K ₂ CO ₃ - 38 Li ₂ CO ₃	11.77

Table 13. Cost of phase-change materials – Part B

Composition, % wt.	Price, €/kg
60 KNO ₃ - 30 LiNO ₃ - 10 Ca(NO ₃) ₂	11.72
67 KNO ₃ - 33 LiNO ₃	12.87
61 NaOH - 39 NaNO ₂	0.82
90.8 LiNO ₃ - 9.2 Ba(NO ₃) ₂	33.85
40.4 NaOH - 59.6 NaNO ₃	0.63
85.8 NaOH - 7.8 NaCl - 6.4 Na ₂ CO ₃	0.67
59.7 NaOH - 24.7 NaCl - 15.7 Na ₂ CO ₃	-
86.3 NaNO ₃ - 8.4 NaCl - 5.3 Na ₂ SO ₄	0.50
5 NaBr-25 KBr- 55 LiBr- 15CaBr ₂	4.45
4.9 LiF -47.8 LiCl - 47.2 LiVO ₃	-
56 KCl - 44 LiCl	6.48
22.9 KCl - 60.6 MnCl ₂ - 16.5 NaCl	1.01
71.8 KCl - 28.2 LiCl	4.37
68.2 MgCl ₂ -14.0 NaCl - 17.8KCl	0.45
55 MgCl ₂ - 24.5 NaCl - 20.5 KCl	0.43
64 MgCl ₂ - 36 KCl	0.52
48.8 MnCl ₂ - 38.1 KCl - 13.1 NaCl	0.94
50 MgCl ₂ - 30 NaCl - 20 KCl	0.41
54.6 KCl - 45.4 MnCl ₂	0.96

Table 14. Cost of phase-change materials – Part C

Composition, % wt.	Price, €/kg
64.3 MnCl ₂ - 35.7 NaCl	0.96
78.7 LiOH - 21.3 LiF	19.12
59.6 KCl - 40.4 MgCl ₂	0.53
56.1 MgCl ₂ - 43.9 NaCl	0.34
54 KCl - 46 ZnCl ₂	0.63
75.8 MnCl ₂ - 24.2 KCl	1.20
52 MgCl ₂ - 48 NaCl	0.33
29.2 LiF - 59.1 KF - 11.7 NaF	9.35
74.2 MnCl ₂ - 25.8 KCl	1.19
44.8 NaCl - 55.2 MgCl ₂	0.34
58.5 CaCl ₂ - 41.5 LiCl	5.93
63 LiF - 37 LiCl	22.74
57.8 KF - 42.2 LiCl	6.96
62 K ₂ CO ₃ - 38 Li ₂ CO ₃	11.77
72 CaCl ₂ - 1.5 CaF ₂ - 26.4 NaF	0.42
67 KF - 33 LiF	10.45
56 Na ₂ CO ₃ - 44 Li ₂ CO ₃	13.22
67 CaCl ₂ - 33 NaCl	0.22

The costs were estimated based on quotes from Alibaba.com and Indiamart, as obtaining quotes for chemical reagents purchased in bulk was challenging due to the lack of available data. Offers for bulk purchase and industrial purity reagents and anhydrous salts were considered. Extremely low and high bids were rejected. It should be noted, however, that the prices presented in Tables 12-14 are primarily for comparison purposes, as shipping costs were not included. In addition, chemical prices vary depending on the purity of the chemicals offered, the vendor, and the quantity. Based on the available data, it was difficult to determine with certainty that all of the substances being priced were of the same purity.

4. Summary and conclusion

Within the framework of task T.5.1. of the HESS project, an extensive review of available materials for energy storage was carried out. A methodology for their assessment was developed. An analysis of energy storage materials was carried out in terms of thermophysical and chemical characteristics, as well as cost and availability. A preliminary selection of materials for further research within the scope of the HESS project was made.

The tables 15-17 present the recommended materials for further research. However, it cannot be ruled out that PCM heat storage materials may be extended/changed for technological or other reasons. Their influence on the granule design and resistance to cycling in heat storage will be investigated.

Table 15. Materials selected as potential energy storage materials at 100 °C

Energy storage material	Justification
Quartzite	Quartzite has a relatively low volumetric heat capacity, but a high thermal conductivity (5.20 W/mK), which facilitates the transfer of heat and the conservation of high temperature potential. Quartzite has previously been proposed as a heat accumulator up to 550°C, which provides structural stability for low-temperature storage. One of the most advantageous properties of quartzite is its low price and wide availability compared to other solid materials.
Rapeseed oil	Rapeseed oil has been defined as a material suitable for low-temperature heat storage. It has the ability to operate between 7 °C and 250 °C, ensuring that it can operate stably even when system operating parameters change. Furthermore, rapeseed oil has a high heat capacity of 2383 J/kgK and a relatively low price of 0.74 €/kg.
48 Ca(NO ₃) ₂ - 45 KNO ₃ - 7 NaNO ₃	The melting point of this PCM is in close proximity to the defined temperature level (120°C), and it is available at a relatively low price (0.57 €/kg) compared to other PCMs with a similar melting point. It exhibits a relatively high hygroscopicity (RH 30-69%), which is comparable to other PCMs with a similar melting point. It is moderately harmful and can cause skin and/or eye irritation, analogous to other PCMs with similar melting points.

Table 16. Materials selected as potential energy storage materials at 300 °C

Energy storage material	Justification
Basalt	Basalt is a material with a wide range of potential applications as a heat-storing material. It exhibits good compressive strength and proven resistance to temperature cycling. Due to its widespread availability, basalt is relatively inexpensive compared to other solid materials, with a cost of 0.11 €/kg. It also has satisfactory volumetric heat capacity value of 2358 kJ/m ³ K and a thermal conductivity of 2.07 W/mK.
Therminol 66	Therminol 66 exhibits a high heat capacity value (2071 J/kgK) and a suitable operating temperature range. It is also more cost-effective (0.93 €/kg) than other thermal oils, which have a higher maximum operating temperature. However, it should be noted that thermal oils are toxic. This fluid is widely used as an energy system integrator and as a heat storage and transfer material.
60 NaNO ₃ – 40 KNO ₃	It is characterized by a melting point of 222°C and high thermal stability (450°C), which allows it to work in a wide range. Heat of conversion is 113-117 kJ/kg. Its toxicity is low. It is relatively inexpensive - €0,69/kg.

Table 17 Materials selected as potential storage materials at 500 °C

Energy storage material	Justification
Basalt	Basalt is a material with a wide range of potential applications as a heat-storing material. It exhibits good compressive strength and proven resistance to temperature cycling. Due to its widespread availability, basalt is relatively inexpensive compared to other solid materials, with a cost of 0.11 €/kg. It also has satisfactory volumetric heat capacity value of 2358 kJ/m ³ K and a thermal conductivity of 2.07 W/mK.
Solar Salt	Solar Salt has the highest maximum operating temperature of the identified fluids, with a capability of 600°C. It exhibits a higher heat capacity value than Hitec XL and a similar thermal conductivity value (0.519 W/mK). Additionally, it is more cost-effective than Hitec XL (0.47 €/kg). Solar Salt is frequently proposed as a potential material for heat storage and utilisation in solar systems.
32.1 Li ₂ CO ₃ – 34.5 K ₂ CO ₃ – Na ₂ CO ₃	The melting point of this material is 400 °C, it is stable up to high temperature (800-850°C), which allows it to work in a wide range. It is characterized by a high heat of fusion of about 257 kJ/kg, an additional - low toxicity. The disadvantage is the high price estimated at 9.89 €/kg.

Furthermore, the research yielded the following findings:

- The recommended materials, as indicated in Tables 15-17 and characterised by favourable thermophysical parameters for heat storage processes, are structurally stable in the relevant temperature ranges and are relatively cheap and readily available. They therefore fit into the concept of an energy storage system using post-mining infrastructure, which is expected to lead to a reduction in capital expenditure.
- The ceramic material (Alferrock) was subjected to experimental testing, which demonstrated its excellent thermophysical performance in terms of heat storage. However, due to its classification as a ceramic material, it is a relatively expensive solution in the context of large-scale energy storage.
- The utilisation of phase-change materials (PCMs) in thermal storage systems gives rise to a number of challenges in maintaining the stability of the heat transfer process. This is particularly evident during the discharge stage of heat storage, when PCM

solidification occurs in proximity to the heat transfer surface. The process of solidification results in a reduction in the heat transfer flux.

- Heat storage in the form of a packed bed causes a significant pressure drop of the flowing HTF. It is necessary that studies on the efficiency of the energy storage system take into account the dynamic effect of changes in the temperature of the packed bed on the value of the pressure drop and, consequently, on the power of the HTF pumps or compressors.
- When using PCMs, it is important to pay attention to additional properties of phase change materials such as hygroscopicity and toxicity. This will have an impact on the use of specific pcm's on a large scale.

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