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1 Sensitivity analysis of thermophysical properties on PCM 2 selection under steady and fluctuating heat sources : A 3 comparative study

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10 HIGHLIGHTS

- 11 ● Effects of PCM thermophysical properties on LTES performance are investigated
- 12 ● Prominent factors for PCM selection under different conditions are specified
- 13 ● PCM selection for LTES under fluctuating heat source condition is studied
- 14 ● The effect of C_p and L on charging rate is reinforced under fluctuating heat source
- 15 ● $\text{LiNO}_3\text{-NaNO}_2$ performs the best under both steady and fluctuating heat sources

16 Abstract

17 Previous studies on phase change material (PCM) selection for latent thermal energy storage (LTES) mainly focused on
18 steady heat source conditions without considering the effects of thermal fluctuation of real heat sources, and how
19 fluctuating heat sources will affect the charging performance of LTES and material selection is still unclear. This study
20 aims to compare the difference in material selection for a shell-and-tube LTES under steady and fluctuating heat sources,

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21 which comprehensively considers the effects of PCM thermophysical properties including the melting temperature,
22 density, specific heat capacity, thermal conductivity and latent heat, as well as their interaction effects. By taking heat
23 storage capacity and charging rate as objectives, orthogonal experiment design and stepwise regression analysis have
24 been conducted to specify the significant factors among these parameters under steady and fluctuating heat source
25 conditions. To further investigate the difference in the ranking of candidate PCMs under two conditions, fourteen pre-
26 screened PCMs are ranked under steady and fluctuating heat sources. The results show that the order of prominent
27 factors for heat storage capacity is $\rho \cdot C_p$, followed by $\rho \cdot L$ under both conditions. However, when considering the
28 charging rate, temperature fluctuation will weaken the effect of melting temperature, and strengthen the effect of specific
29 heat capacity and latent heat. The order of prominent factors for charging rate is $\lambda \cdot C_p$ and $C_p \cdot L$ under fluctuating
30 heat source. According to the ranking results, $\text{LiNO}_3\text{-NaNO}_2$ within the melting temperature of 100-200 °C has an
31 excellent comprehensive charging performance under both conditions.

32 **Keywords:** Latent thermal energy storage, Phase change materials, Multi-criteria decision, Fluctuating heat source, PCM
33 selection

34

Nomenclature

A_{mush}	Porosity function in momentum equations ($\text{kg/m}^3 \text{ s}$)
C	Constant coefficient of porosity function ($\text{kg/m}^3 \text{ s}$)
C_p	Specific heat capacity (J/kg K)
e	The indicator after range normalization
f	Liquid fraction
H	Enthalpy of the PCM (kJ/kg)
h	Heat transfer convection coefficient ($\text{W/m}^2 \text{ K}$)
K	Thermal conductivity (W/m K)
L	Latent heat of PCM (kJ/kg)
l	Length (mm)
Q	Heat storage capacity (kJ)
q	Sensible heat of PCM (kJ)
R_Q	Range of heat storage capacity (kJ)
R_V	Range of charging rate (kJ/s)
r_1	Inner radius of the tube (m)
r_2	Inner radius of the shell side (m)
T	Temperature ($^{\circ}\text{C}$)
t	Time (s)
V	Charging rate (kJ/s)

Greek letters

α	Volumetric expansion coefficient ($1/\text{K}$)
β	Local liquid fraction
ρ	Density (kg/m^3)
λ	Thermal conductivity of PCM (W/m K)
μ	Dynamic viscosity ($\text{Pa}\cdot\text{s}$)
ε	Constant number

Subscript

m	Melting
$HTF-us$	Heat transfer fluid under fluctuating heat source condition
$HTF-s$	Heat transfer fluid under steady heat source condition
F	Heat transfer fluid
us	Fluctuating heat source condition
s	Steady heat source condition
p	Predicted
ref	Reference

Abbreviations

HTF	Heat transfer fluid
LTES	Latent heat thermal energy storage
ORC	Organic Rankine Cycle
PCM	Phase change material
WHR	Waste heat recovery
MCDM	Multiple Criteria Decision Making
TOPSIS	Techniques for Order Preference by Similarity to Ideal Solutions
Rs	The ranking under steady heat source condition
Rf	The ranking under fluctuating heat source condition

35 **1. Introduction**

36 The nature of intermittent and fluctuating thermal sources such as solar, geothermal and industrial waste heat is one
37 of the key research challenges in the development of thermal energy conversion and storage technologies [1-3]. Latent
38 thermal energy storage (LTES) using phase change material (PCM) is a promising solution to minimize the negative
39 effect from fluctuating heat sources [4, 5]. In such a system, LTES using PCM firstly absorbs heat from the heat transfer
40 fluid (HTF) with fluctuating mass flow rate and temperature and then releases the stored heat to waste heat recovery
41 (WHR) systems.

42 With the advantage of PCM having large enthalpy of fusion, this technology has been widely studied in the
43 applications of the solar energy and industrial waste heat. Esen [6] investigated a cylindrical phase change material tank
44 combined with a solar-powered heat pump system by a theoretical model, and the storage can help the heat pump operate
45 at a higher coefficient of performance. Faegh et al. [7] proposed an innovative system using in combination with PCM
46 for desalination. The PCM can recover the latent heat of condensing vapor in solar stills and therefore the waste heat
47 can be stored to recycle. The results demonstrated that the PCM-based solar still can improve the water yield by 86%.
48 Furthermore, Organic Rankine cycle (ORC) system is playing an important role in WHR [8, 9], and ORC integrated
49 with LTES can have great potential of energy saving. Cioccolanti et al. [10] proposed a new small scale concentrated
50 solar ORC using PCM for thermal storage and evaluated the performance of the integrated system by simulation. They
51 have found that high annual operating hours, power production and conversion efficiencies can be achieved by using
52 PCM for storing heat. Dal Magro et al. [11] studied an ORC system combined with a PCM-based technology in steel
53 billet reheating furnace and the results showed that the PCM-based technology allowed an increase of capacity factor
54 by 14% and average thermal efficiency improvement almost by 1%.

55 It can be seen that the heat recovery systems integrated with LTES are recognized as an effective way to address
56 the fluctuation of thermal energy and improve energy efficiency. In order to promote the performance of PCM as retrofit

57 in LTES system, much research has focused on studying the design parameters of LTES system in recent years. Esen et
58 al. [12] compared and investigated the performance of a solar assisted cylindrical energy storage tank with different
59 PCMs. The authors suggested that PCM, cylinder radius, and the inlet temperature and mass flow of HTF can affect the
60 performance of the storage and should be chosen carefully when optimizing the performance. Nie et al. [13] studied the
61 effect of geometry on the performance of the shell-and-tube latent thermal energy storages using pure PCM and
62 composite PCM. The results revealed that the impact of geometry modification on the thermal performance is different
63 with pure and composite PCMs. Compared with cylindrical unit with copper foam of 94.86% porosity, the optimum
64 angle of frustum tube in value with 2° can make complete melting time decrease by 5.9%. And some research [14] have
65 revealed that the PCM melting process depend on not only geometric parameters, but the thermophysical properties of
66 PCM. In fact, different PCMs on account of distinctive properties will take effects on the overall charging performance
67 of LTES. Therefore, it is critical to select an optimal PCM for an exceptional storing performance during the initial
68 phase of the design of LTES system. As for the PCM selection for LTES, the melting temperature of PCMs should be
69 qualified within the operating temperature first. Then the relative importance of the thermophysical properties of PCM
70 will be assessed according to the requirements of specific applications [15]. Thus, the PCM selection criteria for LTES
71 depends on the purpose of real applications. Regarding the fields of solar energy and industrial waste heat recovery,
72 PCM should have great charging performance [16, 17]. The definition of a LTES with excellent performance means the
73 system possesses large heat storage capacity and high charging rate during the charging process. However, these two
74 indicators are generally contradictory [18]. Therefore, PCMs for LTES system need to be carefully selected based on
75 the actual requirements.

76 In fact, PCM selection has been widely discussed in the low-and-medium temperature WHR fields in recent years.
77 For example, Loganathan et al. [19] selected a suitable PCM for thermal management power electronic devices by using
78 the criterial weights of Fuzzy Analytical Hierarchy Process. And this study regarded the melting temperature and latent
79 heat as the most important two factors while selecting. Rastogi et al. [20] aimed to select PCM for keeping the suitable

80 room temperature using LTES, taking two Figures of Merit (FOMs) as objectives, which are $FOM_1=\rho\cdot L$ and
81 $FOM_2=\lambda/(\rho\cdot Cp)$, representing the heat storage capacity and the heat energy transfer rate respectively. The selected
82 optimal PCM can effectively keep the room temperature within the human comfort zone from 21 °C to 26 °C. Tang et
83 al. [21] proposed a practical ranking system to assess superior PCMs for use in buildings. In this analysis, latent heat,
84 melting temperature and thermal conductivity are chosen as evaluation indicators for thermal performance. Above
85 studies demonstrated that a suitable material for buildings and thermal management applications can be fabricated within
86 the desired operating temperature range and have a high latent heat of fusion. But selecting PCM for the higher melting
87 temperature of PCM applications has been paid little attention.

88 In the WHR applications using medium-to-high temperature PCMs, Xu et al. [15] employed the Analytical
89 Hierarchy Process (AHP), which subjectively employed weights of density, latent heat, specific heat capacity, cost, and
90 thermal conductivity in a case study of using LTES system in a cogeneration plant. Then Techniques for Order
91 Preference by Similarity to Ideal Solutions (TOPSIS) method was adopted to rank the candidate PCMs with phase
92 change temperature between 200 °C and 350 °C. Yang et al. [22] combined AHP with the entropy information method
93 taking into account the subjective and objective weighting of the criteria to rank materials used in ground source heat
94 pump integrated with phase change thermal storage system. However, the effect of the PCM melting temperature was
95 not included during the selection process above the two studies. In fact, the melting temperature of PCM can influence
96 the performance of LTES. Li et al. [23] investigated the thermal performance of a solar chimney with PCM and found
97 that phase change temperature greatly influenced the charging rate. For example, when the phase change temperature is
98 decreased by 10 °C, the melt-down time will reduce by almost 50%. Tao et al. [24] revealed the effects of thermophysical
99 properties of molten salt PCM on the heat and exergy storage performance of a shell-and-tube LTES unit. It was found
100 that PCM with a lower melting temperature is beneficial to the improvement of the charging rate and heat storage quality.
101 In summary, when the temperature difference between the heat source and melting temperature of PCM is relatively
102 large, especially for a wider melting temperature range of candidate PCMs, the influence of melting temperature on

103 charging process should be considered while selecting proper PCMs.

104 Meanwhile, waste heat sources with the nature of intermittence and fluctuation in the actual situations, therefore,
105 the heat transfer process of LTES was also investigated under fluctuating heat sources. Huo et al. [25] proposed the
106 heating method which was simplified as time-variant heat flux with square wave for a LTES tank and numerically
107 studied the effects of periods and amplifications for the PCM melting process. The results showed that fluctuating heat
108 flux could reduce the final average temperature and melting time of PCM compared with steady-state heat boundary. Li
109 et al. [26, 27] investigated the dynamic heat transfer characteristics of LTES and the effects of the composite PCM with
110 Al_2O_3 nanoparticles and pure PCM on the melting process under different sinusoidal fluctuating heat sources. It was
111 found that fluctuating heat sources with large fluctuation can significantly accelerate the melting rate and decrease the
112 energy storage capacity of LTES in comparison with the constant heat source. The total melting time and energy storage
113 capacity are reduced by 24.5% and 9.5% when the fluctuating period is 60 min in contrast to that of the constant heat
114 source. The reviewed literature demonstrated that the fluctuation of heat source could bring about a great effect on the
115 charging performance of LTES. It can be inferred that the existing of fluctuating heat sources might lead to the different
116 results of material selection compared with steady heat sources.

117 Based on the above literature, it can be concluded that the effects of thermophysical properties on the PCM selecting
118 process have not been completely revealed on the one hand. For example, the impact of the melting temperature of
119 PCMs on charging performance was less considered in the WHR applications when conducting the PCM selection
120 process, and the correlation effects among thermophysical properties of PCM are still unclear, including thermal
121 conductivity, density, specific heat capacity, melting temperature and latent heat. On the other hand, previous studies
122 have not dealt with the difference in PCM selection between the steady and fluctuating heat sources, and it is an urgent
123 need to understand the effects of thermal fluctuations on the material selection because most of the real heat sources are
124 fluctuating and intermittent. Therefore, this study aims to reveal the difference in PCM selection for a shell-and-tube
125 LTES under steady and fluctuating heat sources, comprehensively considering the effects of thermophysical properties

126 and their interaction. Taking heat storage capacity and charging rate as the objectives of charging performance, the
127 influence of PCM thermophysical properties is analysed by orthogonal design and stepwise regression analysis. Then,
128 common actual materials are taken as an example to examine the difference of ranking under steady and fluctuating
129 conditions. The ranking results obtained by TOPSIS method are validated by pareto solution and simulation, and a
130 sensitivity analysis is also conducted by applying varied weightings to objectives. The results of this study can provide
131 new insights into the influence of heat source fluctuation on the material selection, and benefit the design and
132 optimization of PCM in a shell-and-tube LTES for fluctuating heat source in the future.

133 **2. Methodology**

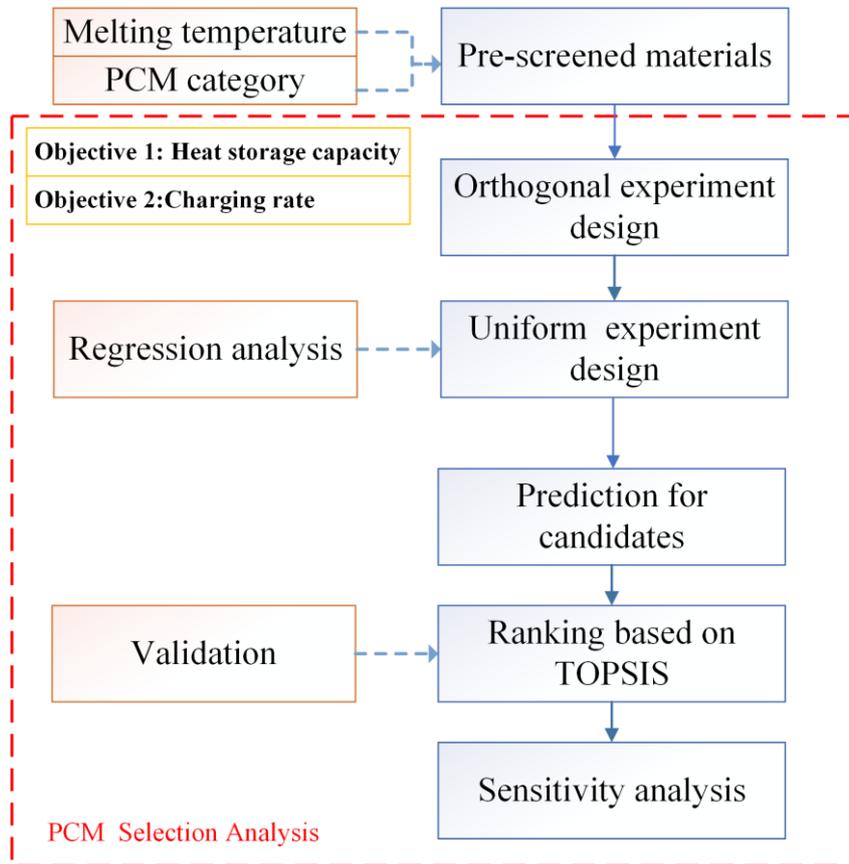
134 To identify the difference in PCM selection between steady and fluctuating heat source conditions, the main
135 methodology adopted in the current study is firstly introduced. Then, the potential PCMs are selected and pre-screened
136 in terms of the operating conditions and applications of the LTES system. Finally, the simulation model of a shell-and-
137 tube LTES heat exchanger was illustrated and validated, and the simulation model would be employed to the following
138 study.

139 **2.1 Selection procedure of phase change material**

140 This work aims to investigate the difference in PCM selection for a shell-and-tube LTES between steady and
141 fluctuating heat source conditions. In the present study, the heat storage capacity and charging rate are used as the key
142 objectives to assess the charging performance of the LTES system during the selecting process. Besides, the following
143 study of the influence of PCM thermophysical properties on LTES performance is explored through the simulation
144 method, and the simulation model is described in detail in Section 2.3. Compared with the inlet temperature fluctuation,
145 the effects of HTF flow rate fluctuation have negligible impacts on the thermal energy storage performance as reported
146 by references [28, 29]. Therefore, the fluctuating heat source condition only considers the temperature fluctuation
147 without giving considerable attention to the mass flow rate change of HTF in this research. Meanwhile, research shows

148 that natural convection could significantly accelerate the PCM charging process [30, 31], so natural convection is
149 considered in this work to ensure the reliability of the results.

150 The flowchart shown in **Fig. 1** illustrates the selection procedure of PCM under steady and fluctuating heat source
151 conditions. Based on the operating conditions and applications of the LTES system, potential candidates are pre-screened
152 by primarily considering the range of melting temperature and availability of the phase change materials. Then, an
153 orthogonal experiment with 5 test factors and 4 levels is designed to do an initial analysis of specifying the difference
154 in single-factor effects between steady and fluctuating heat source conditions. Next, the stepwise regression analysis has
155 been conducted to analyse the interaction effects among PCM thermophysical properties on the heat storage capacity
156 and charging rate. The relationships between these two key objectives and the five thermophysical properties of PCM
157 are represented as multiple nonlinear regression equations using the uniform experiment design method and regression
158 analysis. The obtained equations are applied to predict the charging performance of the actual materials later. The results
159 are used to provide a ranking through TOPSIS method, which is an efficient ranking method developed by Hwang and
160 Yoon [32]. The obtained results are compared to the results from the Pareto front method and simulation to demonstrate
161 the accuracy. Besides, the differences in the charging performance of actual PCMs between the two conditions are
162 analysed. Finally, a sensitivity analysis is conducted by applying various weightings to objective functions.



163
164 **Fig. 1.** Flowchart of the material selection analysis under steady and fluctuating heat source conditions.

165 2.2 Pre-screening of phase change materials

166 Phase change materials such as organic materials, salt and salt composite have been widely used in the LTES
 167 systems [33, 34], due to the relatively large latent heat, adjustable melting temperature and low cost. The pre-selection
 168 principle in this work is focused on the range of heat source temperature (200-400 °C) and the operating temperature of
 169 the WHR system, such as the Organic Rankine cycle. Therefore, some commonly used salts/salt composites and
 170 promising organic PCM are included in a preferred consideration list. In this paper, fourteen popular phase change
 171 materials with melting temperature in the range of 100-200 °C from Ref. [35] are pre-screened to study and the detailed
 172 information is shown in **Table 1**.

174 **Table 1** Thermophysical properties of selected Phase Change Materials [35].

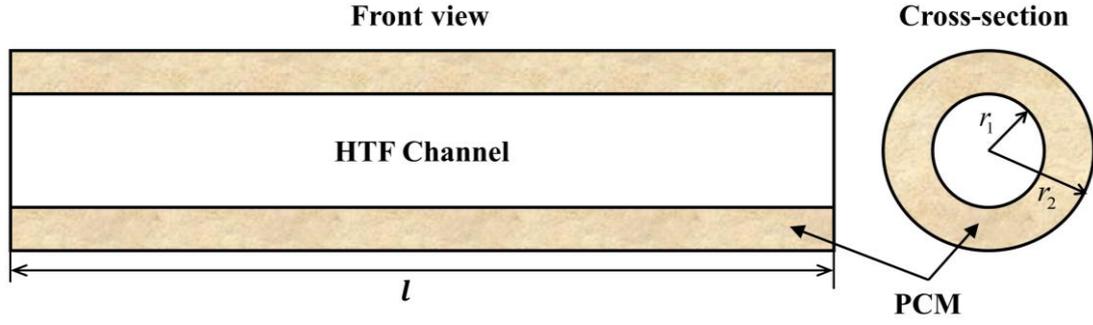
NO.	Candidates	Mass ratio	T_m	ρ	L	C_p	λ
			°C	kg/m ³	kJ/kg	J/(kg·K)	W/(m·K)
1	KNO ₃ -LiNO ₃ -NaNO ₃	52:30:18	123	2068	140	1440	0.53
2	LiNO ₃ -KNO ₃	34:66	133	2018	150	1350	0.52
3	KNO ₃ -NaNO ₂	56:44	141	1994	97	1740	0.57
4	KNO ₃ -NaNO ₃ -NaNO ₂	53:6:41	142	2006	110	1730	0.57
5	KNO ₂ -NaNO ₃	48:52	149	2080	124	1630	0.52
6	LiNO ₃ -NaNO ₂	62:38	156	2296	233	1910	0.66
7	LiNO ₃ -NaNO ₃ -KCL	45:50:5	160	2297	266	1690	0.59
8	LiNO ₃ -KCl	58:42	160	2196	272	1350	0.59
9	HDPE		130	952	255	2150	0.44
10	Urea		134	1320	250	2110	0.60
11	HCOONa-HCOOK	45:55	176	1913	175	930	0.43
12	Urea-NH ₄ Cl	85:15	102	1348	214	2090	0.58
13	Urea-NaCl	90:10	112	1372	230	2020	0.60
14	Urea-K ₂ CO ₃	15:85	102	1415	206	2020	0.58

175 **2.3 Simulation model of a shell-and-tube latent thermal energy storage**

176 The schematic diagram of a shell-and-tube LTES heat exchanger is shown in **Fig. 2**. The PCM placed in the outer
177 layer absorbs the heat released from HTF flowing through the inside. The geometric parameters are defined as follows:
178 the length of the LTES heat exchanger (l) is 1000 mm, and the radius of the inner tube (r_1) and outer shell (r_2) are 12.5
179 mm and 25 mm, respectively. And the inlet temperature of HTF is set at $T_{HTF,s}=300$ °C for steady heat source, while
180 fluctuating heat source is assumed as a sinusoidal fluctuation $T_{HTF,us}=100\cdot\sin(\pi t/1800) +300$ °C. To simplify the
181 mathematical model, the following assumptions are adopted:

- 182 (1) The thickness of the tube wall is not considered;
183 (2) The thermophysical properties of PCM and HTF are independent of temperature except the density of PCM;
184 (3) The axial heat conduction and viscous dissipation in the HTF is neglected and the HTF flow is treated as one-
185 dimensional fluid flow;

186 (4) Due to the symmetry, half of the tube is chosen as the computational domain and with consideration of natural
 187 convection, a two-dimensional cross-section of PCM is selected.



188
 189 **Fig. 2.** Schematic diagram of the shell-and-tube LTES heat exchanger.

190 **2.3.1 Governing equations**

191 A two-dimensional (2-D) transient heat transfer model for the cross-section of a shell-and-tube LTES unit based on
 192 the enthalpy method is presented to simulate the moving boundary problem within the PCM. Firstly, the continuity
 193 equation for PCM is written as follows:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} = 0 \quad (1)$$

194 In the enthalpy method, liquid state and solid state have the same form of the energy equation. The solid-liquid
 195 interface is indicated as a mushy zone to separate two phases. The energy equation for PCM can be described as:

$$\frac{\partial \rho H}{\partial t} + \frac{\partial(\rho u H)}{\partial x} + \frac{\partial(\rho v H)}{\partial y} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k \frac{\partial T}{\partial y} \right) \quad (2)$$

196 Where H represents the total enthalpy of sensible enthalpy and latent enthalpy, which can be calculated by Eq. (3)
 197 and (4). q_{ref} denotes the sensible enthalpy at the reference temperature T_{ref} .

$$H = q + f \cdot L \quad (3)$$

$$q = q_{ref} + \int_{T_{ref}}^T C_p dT \quad (4)$$

198 Where f refers to the liquid volume fraction (the ratio of liquid PCM volume to the total volume of computational
 199 cell) calculated by Eq. (5).

$$f = \begin{cases} 0 & T < T_{solidus} \\ \frac{T - T_{solidus}}{T_{liquidus} - T_{solidus}} & T_{solidus} \leq T \leq T_{liquidus} \\ f = 1 & T > T_{liquidus} \end{cases} \quad (5)$$

200 Substituting Eq. (3) -(5) into Eq. (2), the energy equation can then be written as:

$$\frac{\partial \rho h}{\partial t} + \nabla \cdot (\rho v h) = \nabla \cdot (k \nabla T) - \frac{\partial \rho f L}{\partial t} - \nabla \cdot (\rho v f L) \quad (6)$$

201 The existence of natural convection will promote the increase of sensible heat and accelerate the melting process

202 [36]. With consideration of the small variation in density, the natural convection is taken into consideration via the

203 Boussinesq approximation [37], which is:

$$(\rho - \rho_0)g = -\rho_0\beta(T - T_0) \quad (7)$$

204 And the momentum equation considering natural convection for PCM is:

$$\frac{\partial(\rho u)}{\partial t} + \frac{\partial(\rho u u)}{\partial x} + \frac{\partial(\rho u v)}{\partial y} = -\frac{\partial \rho}{\partial x} + \frac{\partial}{\partial x} \left(\mu \frac{\partial u}{\partial x} \right) + \frac{\partial}{\partial y} \left(\mu \frac{\partial u}{\partial y} \right) + A_{mush} u \quad (8)$$

$$\frac{\partial(\rho v)}{\partial t} + \frac{\partial(\rho u v)}{\partial x} + \frac{\partial(\rho v v)}{\partial y} = -\frac{\partial \rho}{\partial y} + \frac{\partial}{\partial x} \left(\mu \frac{\partial v}{\partial x} \right) + \frac{\partial}{\partial y} \left(\mu \frac{\partial v}{\partial y} \right) + A_{mush} v + \rho g \alpha (T - T_m) \quad (9)$$

205 In fact, $A_{mush} u$ and $A_{mush} v$ are momentum dissipation source items, which are used for suppressing velocity in the

206 solid and mushy region. In Eq. (9), the parameter A_{mush} is “porosity function” by Brent et al. [38] definition and it is a

207 constant calculated by Eq.(10) to describe how fast the velocity is decreased to zero when the PCM solidifies.

$$A_{mush} = -C \frac{(1-f)^2}{f^3 + \varepsilon} \quad (10)$$

208 Where $C = 1.0 \times 10^5$ is a mushy zone constant to reflect the melting front morphology, f is local liquid fraction

209 which lies between 0~1 in the mushy zone, and $\varepsilon = 0.001$ is a small number to prevent division by zero. The simulation

210 model has been built in ANSYS/Fluent 14.5.

211 2.3.2 Initial and boundary conditions

212 The initial condition for PCM is:

$$t = 0, T_{PCM}(x, y) = 298.15K \quad (11)$$

213 The boundary condition for HTF is:

$$r = r_1, T_f = T_{f,in} \quad (12)$$

214 The boundary condition for the outer wall is:

$$r = r_2, \frac{\partial T_{PCM}}{\partial r} = 0 \quad (13)$$

215 The boundary condition for the inner wall is:

$$u = v = 0, r = r_1, h_f (T_f - T_{PCM}) = -\lambda \frac{\partial T_{PCM}}{\partial r} \quad (14)$$

$$h_f = \frac{\left(\frac{f}{8}\right) \cdot (Re - 1000) Pr}{1 + 12.7 \sqrt{\frac{f}{8}} \left(Pr^{\frac{2}{3}} - 1\right)} \cdot \frac{k}{2r_1} \quad (15)$$

216 Where h_f is the forced convection heat transfer coefficient of HTF in the inner tube.

217 2.3.3 Model validation

218 Three mesh sizes of 0.5 mm, 0.8 mm and 1 mm are used to identify the grid independence, which is corresponding
219 to the grid number of 6006, 2384 and 1580. **Fig. 3** shows the results of the verification of time step and grid size and the
220 result of using 0.8 mm as mesh size is enough to ensure the accuracy of the numerical calculation, which has no
221 significant change compared with 0.5 mm with a relative deviation of 0.75%. Different time steps, including 0.5 s, 1 s,
222 2 s, and 5 s, are also considered to ensure that the selected time step does not affect the computational results based on
223 the mesh size of 0.5 mm. The relative deviation of the liquid fraction is small, which is approximately only 0.05%, when
224 the time step is between 0.5 s and 1 s. Based on the verification results, a mesh size of 0.8 mm and a time step of 1s are

225 used in the subsequent calculation. To meet the convergence criterion, the maximum iterations number in each time step
226 is 400.

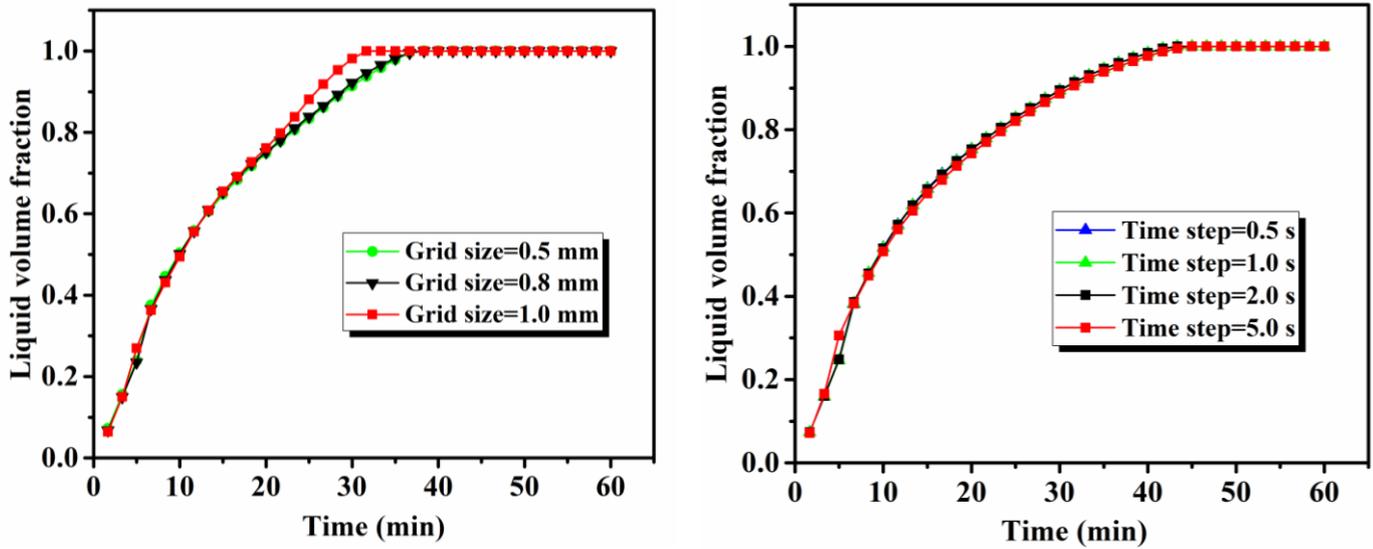


Fig. 3. Validation of the computational time step and grid size: (a) grid size; (b) time step [27].

227 Under the same conditions, the numerical prediction results are compared with the experimental results from Ref
228 [39] to validate the numerical model shown in Fig. 4. In the experimental setup, two thermocouples T_1 and T_2 were
229 placed inside the PCM with the coordinates of $(x = 0.51 \text{ m}, r = 0.002 \text{ m})$ and $(x = 0.95 \text{ m}, r = 0.001 \text{ m})$. The inlet
230 temperature and the mass flow rate of HTF are set at 310.7 K and 0.0315 kg/s, and the initial temperature of PCM takes
231 the value of 282.7 K. It can be seen that the simulated PCM temperature values of the reference points are in close
232 agreement with the experimental values with an error of less than 4.67%. The validation results have proved the precision
233 and reliability of the simulation model.

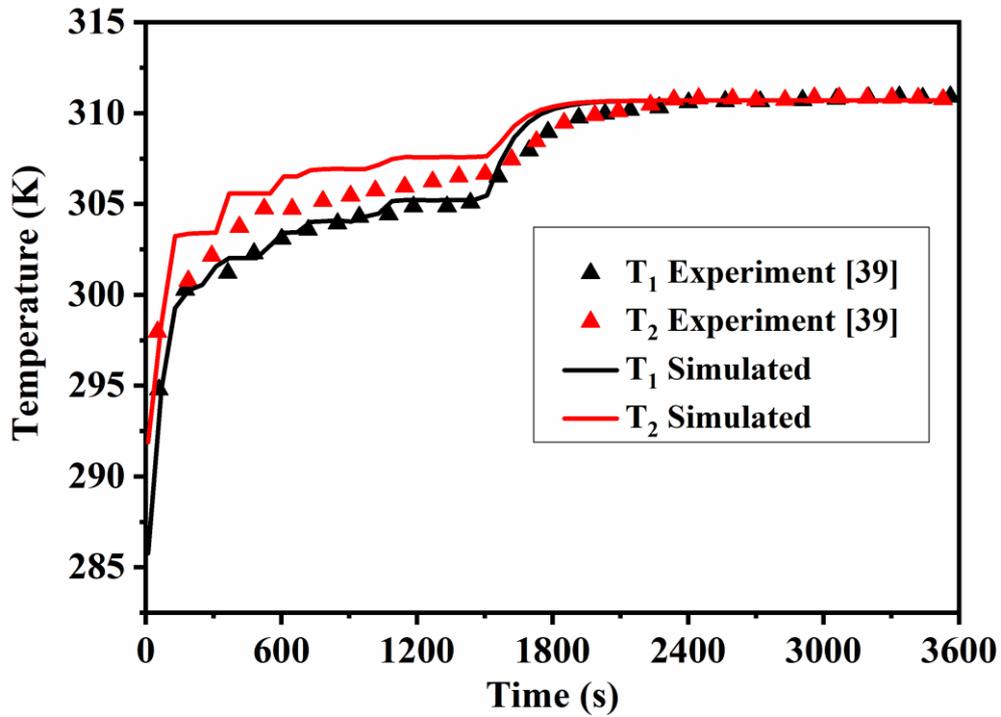


Fig. 4. The simulation model validation results [39].

3. Results and discussion

This section first investigates the influence of the thermophysical properties of PCM on the heat storage performance under steady and fluctuating heat sources, and then conducts the selection study of the actual materials under both conditions. The following table demonstrates the analysis process and the description of methods.

Table 2 The guideline of the conducted tests for the material selection analysis.

Tests	Description
Single-factor effects of PCM thermophysical properties	<ul style="list-style-type: none"> ● Adopt the Orthogonal experiment and range analysis to reveal the single-factor effects of PCM thermophysical properties on LTES performance
Factor interaction effect and prediction	<ul style="list-style-type: none"> ● Consider the factor interaction effect and build the relationships between the objectives and factors by Uniform Design and regression analysis
The ranking of phase change materials	<ul style="list-style-type: none"> ● Based on the two objectives (heat storage capacity and charging rate), use TOPSIS method to rank candidate materials
Results validation	<ul style="list-style-type: none"> ● Conduct the Pareto optimization and the specific simulation study to evaluate and verify the ranking results
Sensitivity analysis of ranking	<ul style="list-style-type: none"> ● Consider different importance degrees of the two objectives

241 3.1 Single-factor effects of thermophysical properties of PCM

242 An orthogonal experiment is conducted to investigate how each factor of PCM thermophysical properties affects
243 LTES performance, including density, thermal conductivity, specific heat capacity, latent heat, and melting temperature.
244 The range of each factor depends on the properties of the candidate PCMs. $L_{16}(4^5)$ orthogonal arrays were selected,
245 where L is the mark of the orthogonal table, 16 is line number of orthogonal table, 5 is level of each factor and 4 is
246 column number of the orthogonal table. The designed scheme is shown in **Appendix A**. To reveal the single-factor
247 effects of PCM thermophysical properties, the heat storage capacity at different times and the average charging rate
248 during the melting process were discussed by range analysis. And in range analysis, K_{ij} stands for the average value of
249 the results of each factor and each level, and k_{ij} equals K_{ij} divided by the number of levels and the value of R_j is the
250 difference between maximum average value $k_{j(\max)}$ and minimum average value $k_{j(\min)}$. The greater the range R is, the
251 larger influence this factor has on the experimental index. Therefore, the magnitude of R can be used to judge the
252 influence of factors.

253 **Fig. 5** demonstrates the relationship between the heat storage capacity with melting time under steady and
254 fluctuating heat source conditions. And under both conditions, the density (ρ) exerts the most significant impact on heat
255 storage capacity among the five factors, followed by the specific heat capacity (C_p), latent heat (L), melting temperature
256 (T_m) and thermal conductivity (λ), i.e., the order is $\rho > C_p > L > T_m > \lambda$. As for steady heat source, the R_Q of density, specific
257 heat capacity and latent heat ascend almost linearly with time. The influence of T_m increases in the first half period, but
258 then decreases gradually during the rest of melting time. On the other hand, the influence of λ is relatively minor among
259 the five factors, but its effect continues to increase with melting time. This is because the initial temperature difference
260 between the heat source and PCM can accelerate the PCM melting at the beginning, while the effect of thermal
261 conductivity will enhance in the last melting process.

262 As a comparison, the values of R_Q in density and specific heat capacity increase first and then level off around 2000
263 kJ from 1800 s to 3600 s under fluctuating heat source condition. The reason is that the heat storage capacity reaches

264 the saturation state in the later melting process, so the effects of ρ and C_p become stable. Additionally, the turning points
 265 of λ and T_m appear earlier 900 s than that of the steady heat source, because fluctuating heat source will promote the
 266 PCM melting. In general, for storage capacity, there is little difference between the two conditions. The R_Q of specific
 267 heat capacity has a slight decline from 1193 kJ to 1131 kJ, so the influence of specific heat capacity is slightly reduced.
 268 However, the influence of latent heat is relatively stronger under fluctuating heat source condition compared steady
 269 condition.

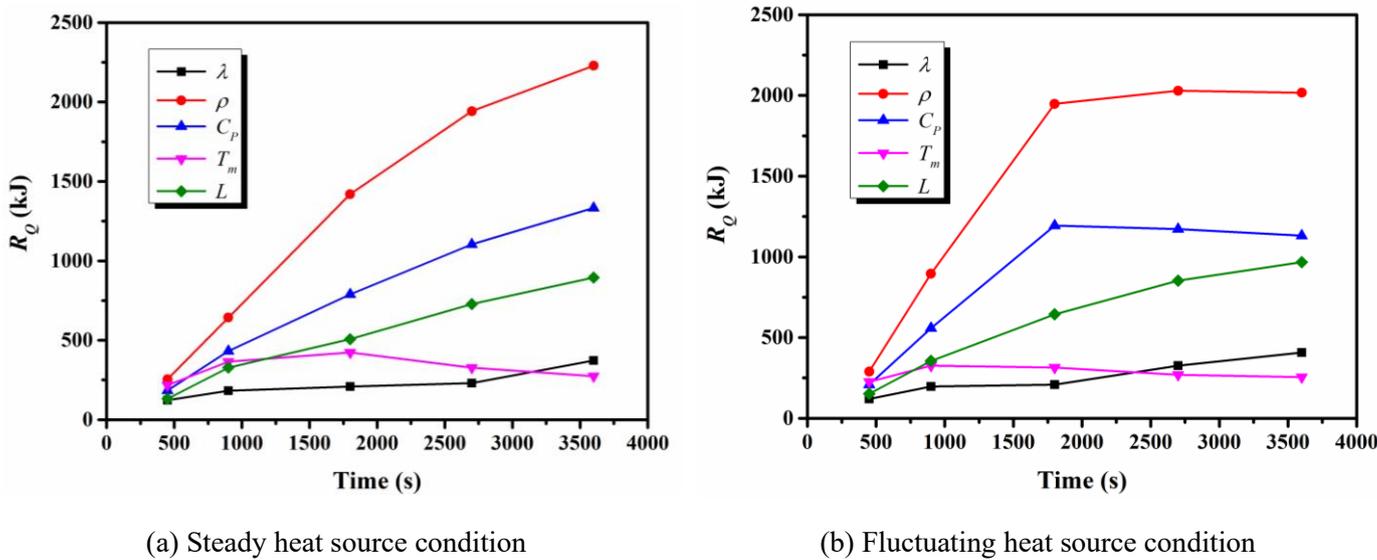


Fig. 5. Relationship between heat storage capacity and melting time.

270 Fig. 6 shows the impact of different PCM thermophysical parameters on the average charging rate of the charging
 271 process. Results indicated that the impact order of five factors is $T_m > \lambda > L > C_p > \rho$ for both conditions, but the value
 272 difference of R_v between density, specific heat capacity and melting temperature gets closer under fluctuating heat source
 273 compared with steady heat source, which indicates that ρ and C_p exert more significant effects on charging rate under
 274 fluctuating heat source. The cause might be the temperature fluctuation facilitates the melting process, so the sensible
 275 heat mainly takes effect. Although melting temperature and thermal conductivity are not important for heat storage
 276 capacity, their effects on the charging rate are highly influential. To further investigate the factor interaction for PCM
 277 selection, the detailed relationship between factors and objectives should be established. Therefore, uniform design
 278 combined with regression analysis will be conducted in the following section.

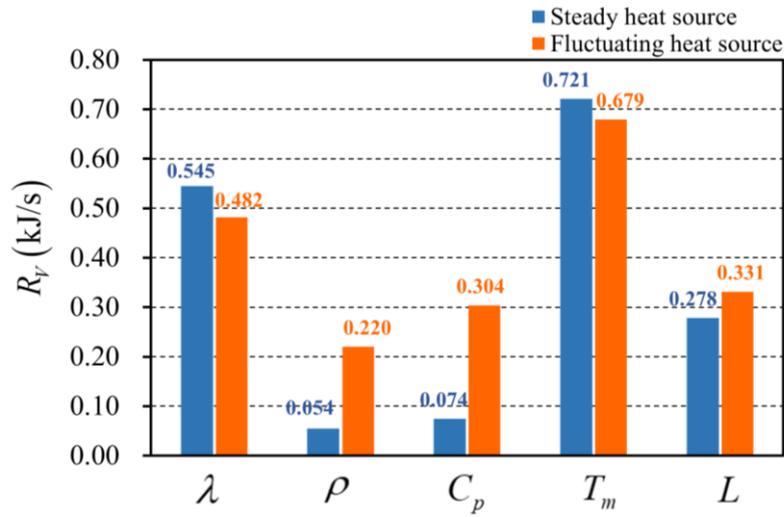


Fig. 6. The impacts of PCM thermophysical properties on the charging rate.

279 3.2 Factor interaction effect and prediction based on regression analysis

280 The Uniform Design (UD) method has been developed based on “Probability Theory”, “Mathematical Statistics”
 281 and “Statistical Experimental Design” as reported in the Ref. [40]. In a uniform design of experiment, experimental
 282 trials are uniformly arranged within the designed scopes of investigated parameters. The maximum information is
 283 obtained by the uniform design with fewer tests, which is based on the test point “uniform dispersion” [41, 42]. Uniform
 284 design tables can be described as $U_n(q^m)$, where U , n , q and m respectively represent the UD, the number of experimental
 285 trials, the number of levels and the maximum number of factors. In this work, the five thermophysical parameters are
 286 chosen as five variables. Thirty levels for each factor are selected to investigate the influence and interaction of the
 287 factors. To improve accuracy, the experiment was carried out using $U_{30}(30^5)$ which was designed by DPS software.

288 The range of each factor arranged is the same as that in the orthogonal experiment and the guide for using $U_{30}(30^5)$
 289 is listed in **Appendix A**. It is worth noting that the two objectives are heat storage capacity (Q) and charging rate (V). Q
 290 represents the heat storage potential of the material. The total charging time is set at 3600 s to ensure that the material
 291 can be completely melted, while V denotes the average heat storage rate during the melting process, which takes the
 292 effect of the material melting rate into account. Based on the results of UD, it can be observed that Q_{us} is lower than Q_s ,
 293 but V_{us} is higher than V_s because PCM melts faster as it is affected by the rising temperature in the first half period under
 294 fluctuating heat source condition. However, in the second period, due to the drop in the temperature of the fluctuating

295 heat source, the heat storage of sensible heat is at a disadvantage. To achieve the optimal regression model, which can
 296 describe the accurate relationship between the two objectives and these properties parameters, a quadratic polynomial
 297 stepwise regression analysis is accomplished by MATLAB. The commonly useful quadratic model is expressed as
 298 follows:

$$y = a_0 + \sum_{k=1}^5 b_k x_k + \sum_{i,j=1}^5 b_{ij} x_i x_j \quad (16)$$

299 Where b_k and b_{ij} are the unknown values that can be calculated by the simulation data based on the least square
 300 method. y indicates the value of the heat storage capacity or charging rate.

301 The basic idea of stepwise regression is to fit a series of regression equations in order. The latter regression equation
 302 is to add or delete an independent variable based on the previous regression equation. Finally, the variables in the
 303 regression equation are significant ($p < 0.05$). Regression analysis of Q and V under steady and fluctuating heat source
 304 conditions can be represented as the following equations:

$$V_s = 1.151 + 2.196\lambda - 5.347e^{-3}T_m - 2.417e^{-3}\lambda \cdot T_m + 6.886e^{-8}\rho \cdot C_p - 2.14e^{-7}\rho \cdot L - 1.548e^{-6}T_m \cdot L - 0.7482\lambda^2 \quad (R^2=0.996) \quad (17)$$

$$Q_s = 137.061 + 9.576e^{-2}\lambda \cdot \rho + 5.569e^{-4}\rho \cdot C_p + 2.056e^{-3}\rho \cdot L \quad (R^2=0.990) \quad (18)$$

$$V_{us} = 2.429 - 7.986e^{-3}T_m + 1.857e^{-3}L + 7.542e^{-4}\lambda \cdot C_p - 1.731e^{-6}C_p \cdot L \quad (R^2=0.904) \quad (19)$$

$$Q_{us} = 190.639 + 4.937e^{-4}\rho \cdot C_p + 2.149e^{-3}\rho \cdot L - 3.62e^{-4}T_m \cdot C_p \quad (R^2=0.995) \quad (20)$$

305 The values of R^2 for the heat storage capacity and charging rate show that the second-order polynomial model is
 306 significant and fits the data results well. In the multiple regression equation, the partial regression coefficient shows the
 307 specific effect of X_j on y_j , but in general, the value of b_k and b_j are affected by the unit of factor. Therefore, the
 308 standardization of the partial regression coefficient can directly determine the importance of each regressor to the test
 309 result y , which is calculated by Eq. (21). The greater the regression coefficient is, the more important it is to the
 310 corresponding factor. The standardised coefficients (P_j) of Eq. (17) - (20) are compared in **Table 3** to analyse which

311 regressor has a greater impact on the objectives under these two conditions. The values of standard regression
 312 coefficients are listed in descending order.

$$P_j = |b_j| \sqrt{\frac{\sum_{j=1}^m (X_j - \bar{X}_j)^2}{\sum_{j=1}^m (y_j - \bar{y})^2}} \quad j = 1, 2, \dots, m; \quad b_j = b_k, b_{ij}; \quad X_j = x_k, x_i x_j \quad (21)$$

313 **Table 3** Standard regression coefficients of regression expressions.

V_s		Q_s		V_{us}		Q_{us}	
<i>Regressor</i>	P_j	<i>Regressor</i>	P_j	<i>Regressor</i>	P_j	<i>Regressor</i>	P_j
λ	1.523	$\rho \cdot C_p$	0.696	$\lambda \cdot C_p$	0.937	$\rho \cdot C_p$	0.686
λ^2	0.731	$\rho \cdot L$	0.423	$C_p \cdot L$	0.853	$\rho \cdot L$	0.491
T_m	0.556	$\lambda \cdot \rho$	0.050	T_m	0.606	$T_m \cdot C_p$	0.036
$\lambda \cdot T_m$	0.304			L	0.431		
$\rho \cdot C_p$	0.294						
$\rho \cdot L$	0.150						
$T_m \cdot L$	0.081						

314 Combined with **Table 3** and the positive or negative signs in equations, the results demonstrate that the standard
 315 deviation of $\rho \cdot C_p$ is increased by 1 time, and the standard deviation of Q_s is raised by 0.696 times under steady heat
 316 source. Therefore, it can be observed that the factors of $\rho \cdot C_p$ and $\rho \cdot L$, which respectively represent sensible heat and
 317 latent heat, significantly influence the heat storage capacity Q for either steady and fluctuating heat source conditions.
 318 However, the value difference of standard regression coefficients between $\rho \cdot C_p$ and $\rho \cdot L$ is narrowing from 0.273
 319 for steady state to 0.195 for fluctuating state, which means that temperature fluctuation can strengthen the melting
 320 process and the effect of latent heat performs more significant. Moreover, $\lambda \cdot \rho$ and $T_m \cdot C_p$ have less impact under
 321 steady and fluctuating heat sources respectively. As for the charging rate, the difference between the two conditions is
 322 obvious, which is that, for the steady heat source condition, the prominent factor is the thermal conductivity of PCM
 323 with λ and λ^2 . Combined with the influence direction, it can be seen that the impact of λ on the charging rate gradually
 324 rises as a convex function with the increase of λ , and the effect tendency will be weakened as the value of T_m grows

325 due to the term of $\lambda \cdot T_m$. Additionally, T_m and $\lambda \cdot T_m$ also have a relatively large impact with standard regression
326 coefficients of 0.556 and 0.304. However, for the fluctuating heat source condition, the influence is a relatively complex
327 interaction. The factor with the greatest effect is $\lambda \cdot C_p$ with the highest value of 0.937, followed by $C_p \cdot L$, T_m and L .
328 The general conclusions can also be drawn from **Fig. 5** and **Fig. 6**. In both cases, the density, specific heat capacity and
329 latent heat have a significant effect on heat storage capacity, while for charging rate, the effect of specific heat capacity
330 is more obvious under the fluctuating heat source condition, so the interactions with density and latent heat are also
331 highlighted accordingly. Based on the regression expressions, the heat storage capacity and the charging rate of the
332 candidate materials in both conditions can be obtained. The predictions of heat storage capacity and charging rate are
333 shown in **Table 4**, and the values will be calculated by the TOPSIS method for ranking analysis.

334 **Table 4** List of the predicted results of candidates.

No.	Candidates	Q_{s-p}	V_{s-p}	Q_{us-p}	V_{us-p}
1	KNO ₃ -LiNO ₃ -NaNO ₃	2495.548	1.4061	2218.997	1.9336
2	LiNO ₃ -KNO ₃	2376.941	1.3044	2121.225	1.8246
3	KNO ₃ -NaNO ₂	2575.633	1.3880	2230.498	1.9393
4	KNO ₃ -NaNO ₃ -NaNO ₂	2632.751	1.3725	2289.334	1.9139
5	KNO ₂ -NaNO ₃	2658.895	1.2565	2330.932	1.7590
6	LiNO ₃ -NaNO ₂	3824.074	1.3229	3397.633	1.7965
7	LiNO ₃ -NaNO ₃ -KCL	3684.713	1.1734	3322.462	1.6193
8	LiNO ₃ -KCl	3140.030	1.1117	2859.829	1.6217
9	HDPE	1816.058	1.1769	1621.724	1.6291
10	Urea	2442.335	1.3580	2172.606	1.8651
11	HCOONa-HCOOK	1894.811	0.8363	1729.232	1.3686
12	Urea-NH ₄ Cl	2373.872	1.5833	2124.398	2.1521
13	Urea-NaCl	2407.973	1.5216	2155.234	2.0718
14	Urea-K ₂ CO ₃	2406.618	1.5867	2153.702	2.1605

335 3.3 Results of ranking using the TOPSIS method

336 TOPSIS is a Multiple Criteria Decision Making (MCDM) method used for ranking, which has been applied widely
 337 across various applications in many fields such as benefit evaluation, health decisions, and health management [43].
 338 TOPSIS can be used to define the relative importance of different factors. The detailed process is presented in **Appendix**
 339 **B**. The ranking results are given in **Fig. 7** by applying equal weighting to the objectives of heat storage capacity and
 340 charging rate first. From **Fig. 7** (a) and (b), the top-ranked materials are NO.6, 7, 8, 14 and 12, which are $\text{LiNO}_3\text{-NaNO}_2$,
 341 $\text{LiNO}_3\text{-NaNO}_3\text{-KCl}$, $\text{LiNO}_3\text{-KCl}$, Urea- K_2CO_3 , and Urea- NH_4Cl . And it is demonstrated that the overall ranking shows
 342 no significant difference between steady and fluctuating heat source conditions. This is because NO.6, 7, 8 have an
 343 advantage of heat storage capacity, meanwhile, NO. 14 and NO.12 are superior in charging rate under both conditions.
 344 Considering the results in **Table 5** and **Fig. 7**, it can be concluded that $\text{LiNO}_3\text{-NaNO}_2$ is ranked as the top one with a
 345 significant advantage in comprehensive charging performance having the scores of 0.808 and 0.798 under both steady
 346 and fluctuating heat source conditions.

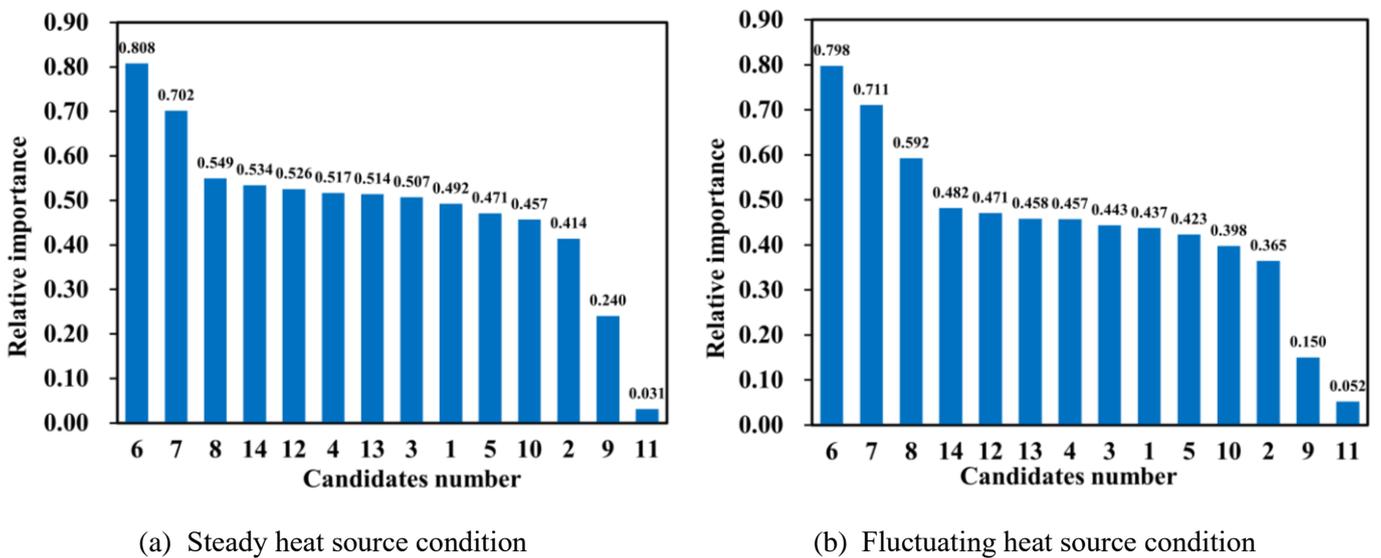


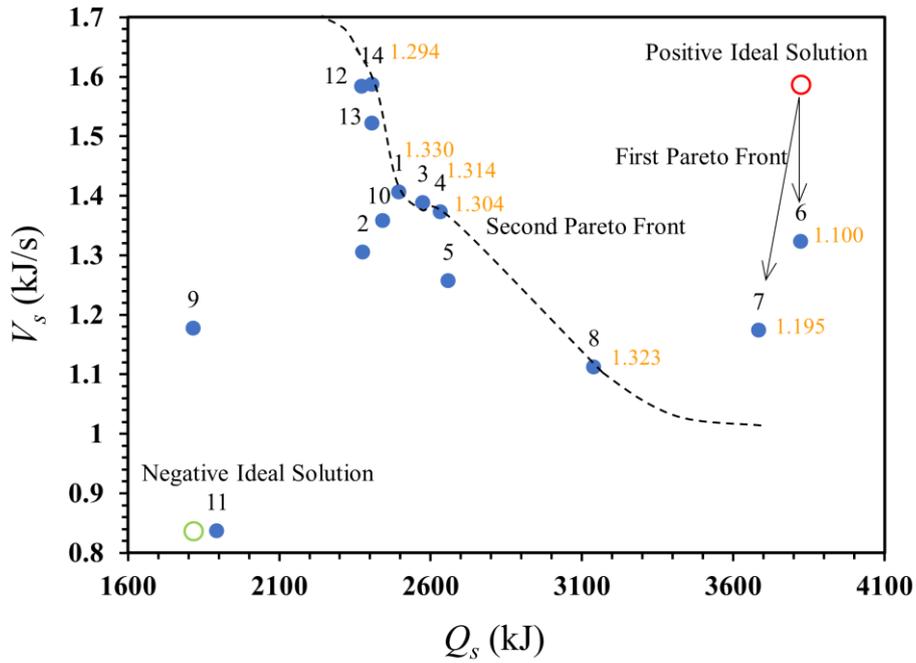
Fig. 7. The ranking of selected PCM under steady and fluctuating heat source conditions.

347 3.4 Validation of ranking results

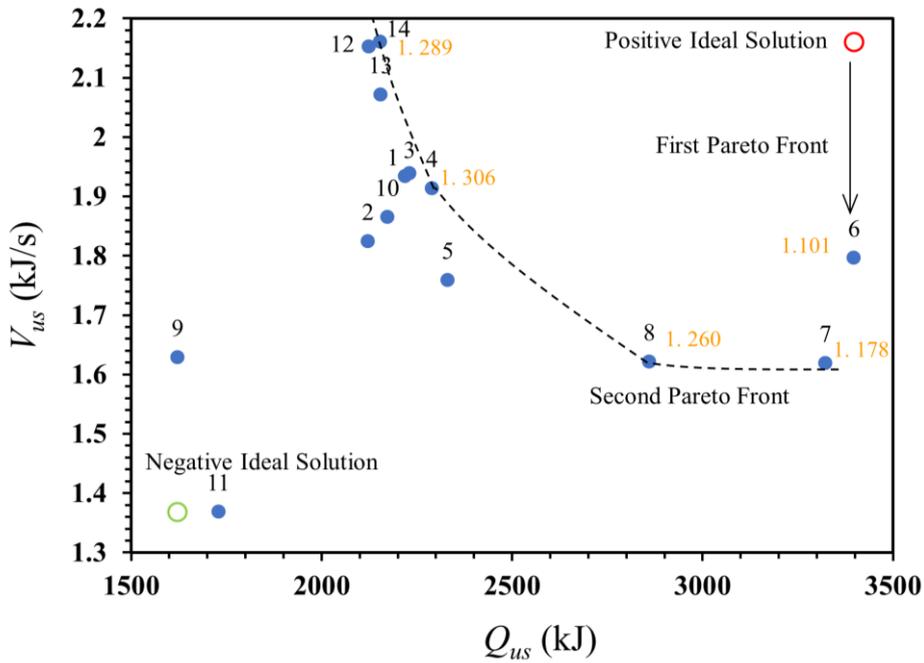
348 The MCDM procedure with Pareto optimization can evaluate the ranking results obtained using the TOPSIS
 349 method [20]. In Pareto solutions, dominated and non-dominated solutions are distinguished. The non-dominated set of

350 the entire feasible decision space is called the Pareto-optimal set which consists of optimal values of all the conflicting
351 attributes. The boundary defined by the set of all points mapped from the Pareto optimal set is defined as the Pareto-
352 optimal front. Hence, the results of the fourteen materials are calculated from the two conflict functions, so they can be
353 plotted into one figure to analyse the relative performance of the material. The materials that are closer to the Positive
354 Ideal Solution and furthest from the Negative Ideal Solution are typically more suitable than other materials. The values
355 of the Positive Ideal Solution and the Negative Ideal Solution in the two attributes come from the highest and lowest
356 heat storage capacity and charging rate of all materials.

357 The materials that are closer to the Positive Ideal Solution and furthest from the Negative Ideal Solution are
358 typically the most suitable choice. The values of the Positive Ideal Solution and the Negative Ideal Solution in the two
359 attributes come from the highest and lowest heat storage capacity and charging rate of all materials. Therefore, the
360 distance from each the Pareto optimal set to the Positive Ideal Solution, which is calculated by $S_i = w_1 \cdot X_p/X_i + w_2 \cdot$
361 Y_p/Y_i referred from [15]. As shown in **Fig. 8**, the distance values displayed near the corresponding materials number.
362 In this equation, w_1 and w_2 means the weights of the two performance objectives. In this study, equal weights are
363 employed to both objectives. Besides, X_p and Y_p are the coordinate values of the Positive Ideal Solution. As shown, NO.6
364 and NO.7 has the shortest distance with value of 1.100 and 1.195 under steady heat source. In view of the first front
365 limited to NO.6 or NO.7 material, a second front is proposed by eliminating them from the solution space to verify the
366 remaining materials. For fluctuating heat source condition, NO.6 and NO.7 stay ahead among the materials because of
367 the higher heat storage capacity. Under both conditions, it can be observed that PCMs NO.2, 10, 9, 5, 11 belong to the
368 dominated solution space which consists of weak solutions in both attributes. The top-ranked materials, NO.6, 7, 8, 14,
369 12 are on the Pareto front which indicates the results obtained from Section 3.3 are aligned well with Pareto optimal
370 solution.



(a) Steady heat source condition



(b) Fluctuating heat source condition

Fig. 8. Examination of materials performance from solution space of attributes.

To further verify the ranking results and analyse the performance of materials in each objective, a simulation study

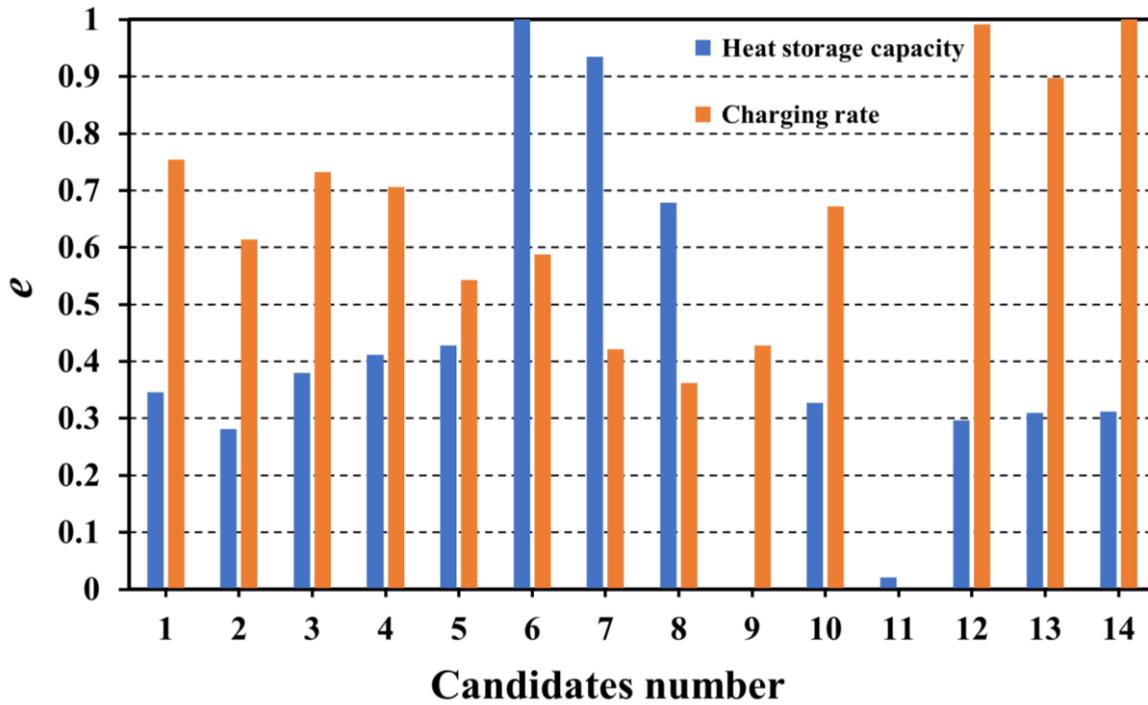
of selected PCM was conducted and the results were plotted in **Fig. 9**. For the comparative analysis, the range

normalization of heat storage capacity and charging rate is carried out respectively. Specifically, the linear

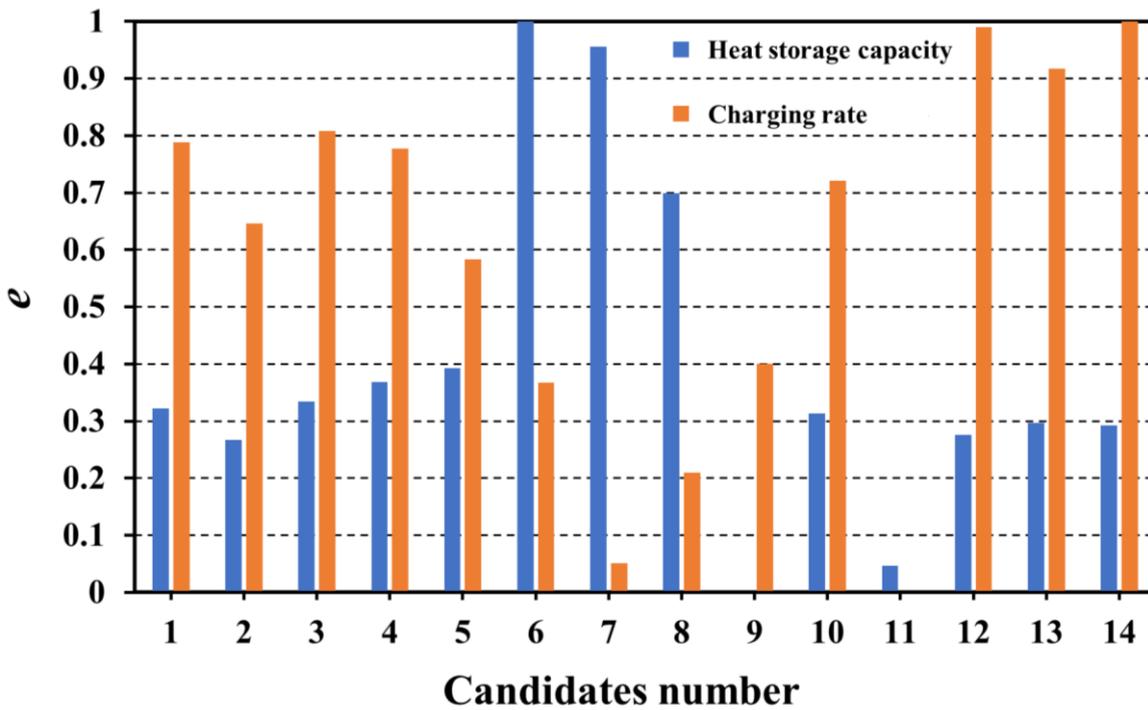
transformation is shaped to the original data x_i , so that the results are within the range of [0,1] denoted by e , which is a

380 positive indicator expressed as $e_i = \frac{(x_i - \min[x_i])}{(\max[x_i] - \min[x_i])}$. **Fig. 9** shows that candidates NO.6, 7, 8 perform better for heat
381 storage capacity, while the candidates NO.14, 12, 13 appear to be excellent in the charging rate and have a stable
382 performance under both conditions, which are in close agreement with the ranking results calculated by TOPSIS method..
383 Combined with Eq. (17) - (20), it can be proved that candidates NO.12, 13, 14, with the characteristics of low melting
384 temperature and high thermal conductivity and specific heat capacity, can maintain a dominant position for charging
385 rate. Additionally, the variance of e_i for heat storage capacity has no difference between the two conditions, so heat
386 storage capacity can barely be affected by the temperature fluctuation.

387 As for the charging rate, it can be concluded from Section 3.2 that not only melting temperature and thermal
388 conductivity, but also latent heat and specific heat capacity has a significant influence. However, the impact of latent
389 heat and specific heat capacity will be covered by melting temperature or other factors, so the overall ranking may
390 remain relatively consistent within the selected materials. Just the ranking of three groups demonstrates distinction,
391 which are NO.5 - NO.6 group, NO.3 - NO.1 group, NO.7 - NO.8 group. The reason is that NO.3 and NO.5 have a lower
392 latent heat, which can accelerate the charging rate under fluctuating heat source. For the candidate material NO.8, the
393 effect of specific heat capacity can also be helpful for its charging rate. Besides, it is worth mentioning that the design
394 optimization criteria of materials will be distinctive under the two conditions inferred from Eq. (17-20). Specifically,
395 when the heat source is relatively steady, PCM with greater thermal conductivity, lower melting temperature and an
396 optimal matching for density, specific heat capacity and latent heat can be beneficial for a good comprehensive charging
397 performance of the LTES. When the heat source temperature varies considerably, the requirements of thermal
398 conductivity and melting temperature are the same as under steady heat source, while density is as large as possible, and
399 there is another optimal matching for specific heat capacity and latent heat.



(a) Steady heat source condition



(b) Fluctuating heat source condition

Fig. 9. The normalization simulation results of selected PCM.

3.5 Sensitivity analysis of ranking

Since the two objectives are usually contradictory, a sensitivity analysis is conducted by applying varied weightings to objective expressions as shown in Table 5. It can examine the difference in the top five orders under steady and

408 fluctuating heat source conditions with consideration of different importance degrees of the two indicators. The
 409 weightings of heat storage capacity and charging rate are respectively set as 0.1:0.9, 0.3:0.7, 0.5:0.5, 0.7:0.3 and 0.9:0.1.
 410 Rs and Rf refers to the ranking under steady heat source and fluctuating heat source respectively. The results indicated
 411 that candidate NO.6, which is $\text{LiNO}_3\text{-NaNO}_2$, offers the best comprehensive charging performance under most
 412 weighting combinations for both conditions. Besides, the molten salt material has a significant advantage in heat storage
 413 capacity, while some Eutectic mixtures with Urea perform better in charging rate, among which Urea- K_2CO_3 is the best.
 414 There is no doubt that the definitive selection criteria of materials should be determined according to the specific
 415 application, namely the heat storage capacity, the charging rate, or the comprehensive performance of LTES. The ranking
 416 results can provide a valuable reference for the selection of PCM in the LTES system.

417 **Table 5** Sensitivity study of ranking under steady and fluctuating heat source conditions.

Weightings ratio (Heat storage: Heat-Charging)	Ranking order	
	Rs	Rf
0.1:0.9	14-12-13-1-3	14-12-13-3-1
0.3:0.7	14-12-6-13-1	6-14-12-13-3
0.5:0.5	6-7-8-14-2	6-7-8-14-2
0.7:0.3	6-7-8-4-5	6-7-8-4-5
0.9:0.1	6-7-8-4-5	6-7-8-4-5

418 **4. Conclusions**

419 This paper has carried out a detailed study on the difference in PCM selection for a shell-and-tube LTES under
 420 steady and fluctuating heat source conditions, considering the effects of melting temperature and factor interaction of
 421 PCM thermophysical properties. The heat storage capacity and charging rate were taken as objectives to assess the
 422 performance of LTES. The parametric study of the LTES performance was investigated under steady and fluctuating
 423 heat sources. On the basis, some actual materials with phase change temperatures of 100-200 °C were ranked by TOPSIS
 424 method and then the verification of ranking results and the sensitivity analysis were performed. Some key findings are
 425 concluded as follows:

- 426 (1) The primary effects on the heat storage capacity are consistent under both heat source conditions, and the order
427 of prominent factors is the interaction of density and specific heat capacity ($\rho \cdot C_p$), followed by the interaction
428 of density and latent heat ($\rho \cdot L$). As for the charging rate, under the steady heat source condition, the order of
429 key factors is thermal conductivity (λ), followed by melting temperature (T_m). And with the increase of
430 thermal conductivity, its influence on the charging rate rises gradually as a convex function and the effect
431 tendency will be weakened when T_m gets higher. However, under fluctuating heat source condition, the
432 product of the thermal conductivity and specific heat capacity and latent heat of PCM have a significant effect,
433 and the order of prominent factors are $\lambda \cdot C_p$, followed by $C_p \cdot L$.
- 434 (2) According to the ranking results, it can be concluded that $\text{LiNO}_3\text{-NaNO}_2$ is the best choice for the heat storage
435 capacity under both heat source conditions, while $\text{Urea-K}_2\text{CO}_3$ indicates excellent performance in the charging
436 rate under both conditions due to its lower melting temperature, larger specific heat capacity and thermal
437 conductivity. As a whole, $\text{LiNO}_3\text{-NaNO}_2$ has an attractive comprehensive charging performance for LTES
438 system.
- 439 (3) To achieve a better charging performance of LTES comprehensively considering the heat storage capacity and
440 charging rate, PCM design and optimization criteria of PCM are different under steady and fluctuating heat
441 source conditions. For steady heat source conditions, PCM should have greater thermal conductivity, lower
442 melting temperature and an optimal balance among the density, specific heat capacity and latent heat. While
443 the higher density and thermal conductivity and lower melting temperature are preferred and a balance
444 between the specific heat capacity and latent heat should be considered for fluctuating heat sources.

445 In the future, the optimization of PCMs under different heat source conditions should be investigated, and the
446 quantitative results of PCM optimal thermophysical properties can be obtained and analysed. In addition, the coupling
447 effect between materials and the geometric parameters of LTES systems should be considered together. Furthermore,
448 more dynamic heat sources and a wider melting temperature range of PCM will be further investigated for extending

449 the scope of this study, digging deeper into the regularity of the influence of dynamic fluctuations of heat sources on
450 PCM selection.

451 **Credit authorship contribution statement**

452 **Xiaoli Yu:** Conceptualization, Methodology, Investigation, Validation, Funding acquisition. **Jinwei Chang:** Writing-
453 Original draft preparation, Methodology, Formal analysis. **Rui Huang:** Supervision, Project administration, Resources.
454 **Yan Huang:** Formal analysis, Data curation. **Yiji Lu:** Writing- Reviewing and Editing, Supervision. **Zhi Li:**
455 Conceptualization, Writing- Reviewing and Editing. **Lei Wang:** Funding acquisition, Project administration, Resources.

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463

464 **Appendix A. Supplementary Tables**

465 **Table A.1** The orthogonal experiment design $L_{16}(4^5)$.

No.	λ	ρ	C_p	T_m	L
1	1	2500	2400	190	370
2	1	1900	1800	160	275
3	1	1400	1350	130	185
4	1	900	900	100	95
5	0.7	2500	1800	130	95
6	0.7	1900	2400	100	185
7	0.7	1400	900	190	275
8	0.7	900	1350	160	370
9	0.5	2500	1350	100	275
10	0.5	1900	900	130	370
11	0.5	1400	2400	160	95
12	0.5	900	1800	190	185
13	0.4	2500	900	160	185
14	0.4	1900	1350	190	95
15	0.4	1400	1800	100	370
16	0.4	900	2400	130	275

466

467 **Table A.2** Uniform design table of $U_{30}(30^5)$ and simulation results.

No.	λ	ρ	C_p	T_m	L	Q_s	V_s	Q_{us}	V_{us}
1	0.71	1783	1883	190	275	3160.59	1.025	2817.75	1.471
2	0.48	1672	1003	171	142	1599.06	0.954	1427.85	1.524
3	0.75	2279	1055	162	304	3097.38	1.173	2838.51	1.732
4	0.59	1562	1676	153	370	2966.34	1.144	2678.10	1.655
5	0.79	1617	2090	100	209	2895.75	1.837	2516.37	2.552
6	0.67	1010	1262	174	342	1588.80	0.986	1480.08	1.575
7	0.69	1948	2400	112	180	3673.96	1.724	3202.76	2.444
8	0.81	1728	1469	134	361	3028.41	1.440	2745.04	2.114
9	0.57	1286	1521	187	190	1784.85	0.938	1575.96	1.562
10	0.42	2114	2038	159	161	3354.24	1.088	2955.99	1.352
11	0.63	1452	2193	147	114	2367.70	1.398	2010.09	2.086
12	0.44	1341	1159	125	218	1663.01	1.157	1501.55	1.677
13	0.73	900	1417	119	152	1106.26	1.518	997.76	1.935
14	0.61	2059	900	116	266	2443.18	1.384	2248.15	1.993
15	0.65	2500	1728	131	247	4033.20	1.457	3605.75	1.937
16	0.86	2224	2245	122	351	4751.08	1.681	4285.44	2.192
17	0.52	955	2297	137	237	1898.27	1.241	1654.82	1.838
18	0.98	1838	1934	128	133	2776.05	1.787	2377.81	2.533
19	0.40	1893	1314	143	285	2810.21	1.020	2532.69	1.382
20	0.92	2445	1366	150	199	3193.64	1.475	2824.18	2.217
21	0.96	1507	1107	106	313	2126.81	1.715	1969.13	2.352
22	0.83	2169	1210	184	123	2278.54	1.186	1981.63	1.926
23	0.90	1397	2348	181	256	2852.25	1.234	2488.30	1.966
24	0.54	2334	1572	103	104	2860.89	1.649	2459.60	2.337
25	0.77	1231	1779	165	95	1634.45	1.342	1397.06	1.955
26	0.50	2390	2141	178	323	4311.13	0.989	3975.65	1.111
27	0.94	1066	1986	156	294	2040.68	1.383	1816.40	2.069
28	0.88	1121	952	140	171	1099.18	1.408	1021.59	1.859
29	0.46	1176	1831	109	332	2272.06	1.301	2030.42	1.870
30	1.00	2003	1624	168	228	3066.99	1.363	2705.08	2.119

468

469 **Appendix B. Techniques for Older Preference by Similarity to Ideal Solutions (TOPSIS)**

470 **method [15]**

471 The principle of TOPSIS is that the alternatives chosen should be as close to the ideal solution as possible and as far

472 away from the negative ideal solution as possible. For each attribute, the ideal solution is from a combination of the best
 473 performance values in the decision matrix, while the negative ideal solution is from a combination of the worst
 474 performance values. The mathematical steps of TOPSIS are as follows:

475 Step 1: Construct decision matrix $A = (a_{ij})_{m \times n}$ of project evaluation which consists of n number of attribute values for
 476 m numbers of alternatives. To get rid of the dimensional effect, $B = (b_{ij})_{m \times n}$ is obtained through normalized
 477 processing.

$$b_{ij} = \frac{a_{ij}}{\sqrt{\sum_{i=1}^m a_{ij}^2}}, \quad i = 1, \dots, m, j = 1, \dots, n \quad (\text{A.1})$$

478 Step 2: According to the contribution of each evaluation index to the evaluation results, different weightings are assigned:
 479 $w = [w_1, \dots, w_n]$. The j^{th} column of B is multiplied by its weighting w_j to obtain the weighted normalized matrix $C =$
 480 $(c_{ij})_{m \times n}$

481 Step 3: Determine the positive ideal solutions C^* and negative ideal solutions C^0

$$C^* = [c_1^*, \dots, c_n^*], \quad C^0 = [c_1^0, \dots, c_n^0] \quad (\text{A.2})$$

482 Where

$$c_j^* = \begin{cases} \max_i c_{ij} \\ \min_i c_{ij} \end{cases}, \quad c_j^0 = \begin{cases} \min_i c_{ij} \\ \max_i c_{ij} \end{cases}, \quad j = 1, \dots, n \quad (\text{A.3})$$

483 Step 4: Calculate the distance from each alternative to the positive and negative ideal solutions.

$$d_i^* = \sqrt{\sum_{j=1}^n (c_{ij} - c_j^*)^2}, \quad i = 1, \dots, m \quad (\text{A.4})$$

$$d_i^0 = \sqrt{\sum_{j=1}^n (c_{ij} - c_j^0)^2}, \quad i = 1, \dots, m \quad (\text{A.5})$$

484 Step 5: Compute the relative importance of each alternative to the ideal solution with the Euclidean distance equation.

485 Finally, arrange f_i in descending order to obtain the relative importance of each evaluation alternative.

$$f_i = \frac{d_i^0}{d_i^0 + d_i^*}, \quad i = 1, \dots, m \quad (\text{A.6})$$

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