Study on the selection method of solid cold energy storage medium for liquid air energy storage

Luna Guo¹,², Wei Ji¹*, Zhaozhao Gao¹,², Xiaoyu Fan¹,², Jianying Hu¹, Liubiao Chen¹, Junjie Wang¹,²

1. Chinese Academy of Sciences Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, 29 Zhongguancun East Road, Haidian District, Beijing, P. R. China.

2. University of Chinese Academy of Sciences, No.19(A) Yuquan Road, Shijingshan District, Beijing, P. R. China.

Corresponding author: jiwei@mail.ipc.ac.cn

Abstract. Liquid air energy storage (LAES) is a promising large-scale energy storage technology. A packed bed cryogenic regenerator was investigated for cold energy storage in the LAES system. As the thermophysical properties of the filling material directly affects the performance of the regenerator, sensitivity analyses of the specific heat capacity and thermal conductivity were carried out. Results show that the thickness of the thermocline in the packed bed can be reduced by increasing the specific heat capacity and decreasing the thermal conductivity. Furthermore, the synergy effect of the specific heat capacity and thermal conductivity on the system was considered. In the case of simultaneous changes of the two parameters, the selection method of the solid material was proposed innovatively, and the feasibility of the method was verified by theoretical calculation of various materials.

1. Introduction

Liquid air energy storage (LAES) is a large-scale energy storage technology not limited by geographical conditions, with high energy storage density and good application prospects [1]. The air liquefaction process is the key of the LAES system, which directly affects the energy storage efficiency of the system. It is particularly important to optimize the performance of the cold energy storage system. As a cold energy storage device, the packed bed filled with solid particles has good performance, safety and environmental protection, and is suitable for use in the LAES system.

Figure 1 shows the schematic diagram of the LAES process. It consists of a compression train, a cold energy storage subsystem and an expansion train. During the charging process, the ambient air is pressurized by compressors and then enters the cold energy storage subsystem to obtain the cold energy of the packed bed. The low-temperature air is further throttled by the throttle valve to produce liquid air stored in the liquid gas tank. During the discharging process, liquid air enters the packed bed to store the cold energy in solid particles, and then expands in turbines to produce electric energy.

At present, there have been many researches on LAES technology using the packed bed. In terms of the overall process, Morgan et al. [2] conducted experiments on a LAES system using the solid material packed bed for cold energy storage, and obtained design and test results on a pilot scale. Sciacovelli et
al. [3] analysed the relationship between components and the system by establishing a dynamic model and validated experimentally. For the packed bed, Chai et al. [4] studied the cold energy storage characteristics of packed beds under different pressure conditions through numerical analysis and experiments. Jin et al. [5] studied the operating performance of the packed bed in multiple continuous cycles, and analysed the effects of the height of the packed bed and the diameter of solid particles on the effective capacity ratio. Because of the dependence of the specific heat capacity on temperature, Hüttermann et al. [6] selected a variety of materials and systematically analysed the effect of the specific heat capacity on cold energy storage performance with low-temperature conditions.

Actually, the performance of the packed bed is affected by the specific heat capacity of the material and is also closely related to the thermal conductivity. There are few studies on the coupling effects of the above two parameters. Therefore, a numerical model was established to analyse the cold energy storage characteristics of the packed bed. The independent and comprehensive effects of the volumetric specific heat capacity and the thermal conductivity of the cold energy storage medium on the system were studied. Considering the synergistic effect of the volumetric specific heat capacity and the thermal conductivity, a selection method of solid materials was proposed. Furthermore, the performance of five actual materials was compared and analysed to verify the practicability and reliability of the proposed selection method.

2. Mathematical model

Figure 2 is a physical model of a packed bed, which is filled with solid particles and covered with insulation material to reduce the cold energy loss. During the cold energy storage process, low-temperature air enters the packed bed from the bottom end, and the cold energy is obtained and stored by the cold energy storage medium. Finally, the temperature of air rises to ambient temperature and flows out from the top of the packed bed.

In order to simplify the analysis, some assumptions are employed as follows:

(1) The solid rock particles are isotropic with the same diameter, the porosity inside the packed bed is uniform, and the tank is symmetrical along the axis;

(2) The physical property parameters of solid particles are selected based on the average temperature of the design temperature zone;

(3) The flow of inlet and outlet is evenly distributed;

(4) The boundary condition of the packed bed is adiabatic.

The heat transfer model is 1D two-phase transient model [7]:

\[(1 - \varepsilon)\rho_s c_{p,s} \frac{\partial T_s}{\partial t} = \nabla \cdot [(1 - \varepsilon)k_s \nabla T_s] + q_{sf}(T_f - T_s)\]

\[ (1) \]
\[ \varepsilon \rho_f c_{p,f} \frac{\partial T_f}{\partial t} + \varepsilon \rho_f c_{p,f} \mathbf{u}_f \cdot \nabla T_f = \nabla \cdot (\varepsilon k_f \nabla T_f) + q_{sf}(T_s - T_f) \]  

(2)

\[ q_{sf} = \frac{6(1-\varepsilon)}{d_p}, h_{sf} = 700G^{0.76}d_p^{0.76} \]  

(3)

where \( \varepsilon \) is the porosity of the solid particles, and \( \rho \) (kg/m\(^3\)) is the density. \( T \) (K) is temperature, and \( t \) (s) is time. \( c_p \) (J/kg\( \cdot \)K\(^{-1}\)) and \( k \) (W/m\( \cdot \)K\(^{-1}\)) are the specific heat capacity and thermal conductivity, respectively, and \( \mathbf{u}_f \) is the velocity vector. \( d_{sf} \) and \( h_{sf} \) are the interstitial convective heat transfer coefficient and interstitial heat transfer coefficient, respectively. \( G \) (kg/s\( \cdot \)m\(^{-2}\)) is the mass flow rate per unit cross section, and \( d_p \) (m) is the particle diameter. The subscripts s and f stand for solid and fluid.

To verify the validity of the model, the same packed bed size, material thermophysical properties and boundary conditions as in the literature [8] are used to compare the simulation results with the experimental results in figure 3, and the relative error is less than 7\%. Thus, the packed bed theoretical model is acceptable.

3. Results and discussions

3.1. Cold energy storage characteristics of the packed bed

Based on the established theoretical model, this section analyses the cold energy storage characteristics of the packed bed. Table 1 lists the basic design parameters. The cold energy storage material is granite particles, and thermal properties of rock are the same as that in references [4] and [9]. Stainless steel and expanded perlite are selected for the wall of the packed bed and the insulation layer, respectively [10]. The inlet temperature is 93.15 K and the air flow rate is 0.1 kg/s.

| Parameter                  | Symbol | Unit      | Value |
|----------------------------|--------|-----------|-------|
| Packed bed Diameter        | \( D \) | m         | 1     |
| Height                     | \( H \) | m         | 4     |
| Wall thickness             | \( D_w \) | m         | 0.016 |
| Insulation layer thickness | \( D_l \) | m         | 0.2   |
| Porosity                   | \( \varepsilon \) | –         | 0.4   |
| Granite particle Density   | \( \rho \) | kg/m\(^3\) | 2688  |

Figure 2. Schematic diagram of the packed bed.

Figure 3. Comparison of simulation and experimental results.

Table 1. Basic design parameters.
Specific heat capacity \( c_p \) kJ/kg·K\(^{-1}\) 0.626
Volumetric specific heat capacity \( s \) kJ/m\(^3\)·K\(^{-1}\) 1682.688
Thermal conductivity \( k \) W/m·K\(^{-1}\) 3.2
Particle diameter \( d_p \) mm 10

The packed bed maintains the ambient temperature (298.15 K) at the initial moment. Low-temperature air (93.15 K) enters from the bottom of the packed bed (\( H=0 \) m), and stores the cold energy in solid particles and flows out from the top (\( H=4 \) m). Figure 4 shows the axial temperature distribution of solid particles in the packed bed. With the continuous transfer of the cold energy, a complete temperature gradient (thermocline) can be formed in the packed bed. As shown in figure 5, the thickness of the thermocline gradually increased from 0.86 m in 0.5 h to 2.76 m in 3 h. When the cold energy storage process lasts for 3 hours, the air temperature at the top outlet begins to drop from the ambient temperature due to the advancement of the thermocline. The solid particles in the packed bed are all cooled to 93.15 K after 6.17 h, and the cold energy storage process is completed. However, the decrease of the outlet air temperature of the packed bed during the cold energy storage process causes the loss of the cold energy. In practice, the outlet air temperature of the cold storage process is limited to 298.15 K instead of the design low temperature (93.15 K), and the process lasts for 3 h.

3.2. Independent influence of the volumetric specific heat capacity and the thermal conductivity

The distribution of the thermocline which is closely related to the thermophysical properties of solid particles has a significant effect on the performance of the packed bed. The independent influence of the volumetric specific heat capacity and the thermal conductivity of solid particles on the cold energy storage performance of the packed bed was analysed in this section, respectively.

Figure 6 shows the thickness of the thermocline with constant thermal conductivity (3.2 W/m·K\(^{-1}\)) and different volumetric specific heat capacities. With the advancement of the cold energy storage process, the thickness of the thermocline gradually increases, and the growth rate is inversely proportional to the volumetric specific heat capacity. When the volumetric specific heat capacity is 1142.4 kJ/m\(^3\)·K\(^{-1}\), the thickness of the thermocline reaches the maximum value of 2.3 m. At 3 h, as the volumetric specific heat capacity increases from 1142.4 kJ/m\(^3\)·K\(^{-1}\) to 2217.6 kJ/m\(^3\)·K\(^{-1}\), the thickness of the thermocline decreases by 0.85 m. In conclusion, increasing the volume specific heat capacity can improve the cold energy storage performance of the packed bed.

Figure 7 illustrates the effect of the thermal conductivity on the thermocline thickness, maintaining the volumetric specific heat capacity of 1682.7 kJ/m\(^3\)·K\(^{-1}\). It can be obtained from the figure that as the
thermal conductivity increases, the thickness of the thermocline increases at different times, and the amount of change gradually increases. When the thermal conductivity is 4.2 W/m·K⁻¹, the thickness of the thermocline increases by 2.05 m from 0.5 h to 3 h. With the thermal conductivity of 2.2 W/m·K⁻¹ and 4.2 W/m·K⁻¹, the maximum thickness of the thermocline can reach 2.4 m and 3 m, respectively. Therefore, reducing the thermal conductivity promotes the reduction of the thickness of the thermocline and the improvement of the cold energy storage performance of the packed bed.

3.3. Coupling influence of the volumetric specific heat capacity and the thermal conductivity
Combined with section 3.2, the thickness of the thermocline can be reduced by increasing the volumetric specific heat capacity or decreasing the thermal conductivity. If the volumetric specific heat capacity and thermal conductivity increase or decrease simultaneously, the coupling effects need to be comprehensively analysed.

In order to comprehensively evaluate the influence of the volumetric specific heat capacity and thermal conductivity and obtain a selection method for solid materials, a physical property curve shown in figure 8 is obtained by simulation calculation. Specifically, using granite as the reference material, by calculating the temperature distribution of the packed bed with different volumetric specific heat capacities and thermal conductivity, multiple sets of parameter combinations are obtained, which are similar to the temperature distribution of the packed bed using granite as the filling material. The thickness of the thermocline is used as a quantitative standard for the temperature field. In the coordinate system, multiple sets of parameter combinations are connected to get a physical property curve (the black line in figure 8). As the volumetric specific heat capacity increases, the thermal conductivity increases approximately linearly. When the volume specific thermal capacities are 1142.4 kJ/m³·K⁻¹, 1411.2 kJ/m³·K⁻¹, 1948.8 kJ/m³·K⁻¹ and 2217.6 kJ/m³·K⁻¹, the corresponding thermal conductivity are 2.0 W/m·K⁻¹, 2.6 W/m·K⁻¹, 4.0 W/m·K⁻¹ and 4.8 W/m·K⁻¹, respectively. At the end of the cold energy storage process, the thickness of the thermocline of the packed bed with five physical property combinations is equal (2.8 m).

In the LAES system, most of the solid materials for cold energy storage are non-metallic materials such as rocks, and the average volumetric heat capacity in the working temperature zone is in the range of 1450-2200 kJ/m³·K⁻¹ [6],[9]. Five materials including dolomite, sodium chloride, concrete, red brick and glass are selected to verify the feasibility of material screening with reference to the physical property line.

The specific steps of using the method are as follow:
(1) According to the volumetric specific heat capacity and thermal conductivity of the material, the coordinates in figure 8 are determined;
(2) The projection distance of the coordinate point along the ordinate direction to the physical property
line \( (\Delta d_i) \) is measured, where \( \Delta d_i = d_i - d_0 \);

(3) The cold energy storage characteristic of the material is evaluated based on the relationship and distance between the coordinate points and the physical property line.

For two materials, if two coordinate points are distributed on both sides of the physical property line, the material performance on the lower right side of the physical property line is better. If the two coordinate points are distributed on the same side of the physical property line, the smaller \( \Delta d_i \), the better the cold energy storage performance of the material.

\[ \text{Figure 8. Correspondence between the volumetric specific heat capacity and thermal conductivity.} \]

Figure 9 is the coordinate values of five materials: dolomite, sodium chloride, concrete, red brick and glass. And figure 10 shows the thickness of the thermocline calculated by the theoretical model for five materials. In figure 9, dolomite and sodium chloride are located on the upper left of the physical property line, and the distance \( \Delta d_i \) between the coordinate point of dolomite and the physical property line along the ordinate direction is greater than that of sodium chloride.

Because the material with smaller \( \Delta d_i \) has better cold energy storage performance, it can be inferred that sodium chloride has better performance than that of dolomite, but both are worse than granite. Concrete, red brick and glass are located below the physical property line. Similarly, it can be concluded that the order of cold energy storage performance from good to poor is: glass, red brick and concrete. As shown in figure 10, the thickness of the thermocline of dolomite with the largest \( \Delta d_i \) is 3.50 m at 3 h, while the thickness of the thermocline of glass with the smallest \( \Delta d_i \) is only 0.88 m. With the increase of \( \Delta d_i \), the thickness of the thermocline increases and the cold energy storage performance deteriorates.

The conclusions obtained in figure 10 are consistent with the results derived in figure 9 based on the selection method. The order of the cold energy storage performance of the five materials from good to bad is: glass, red brick, concrete, granite, sodium chloride and dolomite. The unanimous conclusion confirms the feasibility and versatility of the solid selection method. However, it should be noted that when the coordinates of the two materials are located on the same side of the physical property line and the \( \Delta d_i \) corresponding to the two materials are similar, using the above method has errors. It can be further improved by adding multiple sets of physical property lines.
4. Conclusion

The energy storage performance of the packed bed used in the LAES system was analyzed. When the cold energy storage process lasted for 3 h, the outlet air temperature began to drop from 298.15 K. To further improve the cold energy storage performance, it can increase the volume specific heat capacity of the solid material and reduce the thermal conductivity. Furthermore, for materials whose the volumetric specific heat capacity and thermal conductivity increase or decrease simultaneously, a method of selection materials was proposed. And five actual materials were used to successfully verify the practicability of the selection method.

5. References

[1] Cyrine Damak, Denis Leducq, Hong Minh Hoang, Daniele Negro, Anthony Delahaye. Liquid Air Energy Storage (LAES) as a large-scale storage technology for renewable energy integration—A review of investigation studies and near perspectives of LAES. Int. J. Refrig. 2020, 110: 208-18.

[2] Robert Morgan, Stuart Nelmes, Emma Gibson, Gareth Brett. Liquid air energy storage-analysis and first results from a pilot scale demonstration plant. Appl Energy 2015; 137: 845-53.

[3] A. Sciacovelli, A. Vecchi, Yulong Ding. Liquid air energy storage (LAES) with packed bed cold thermal storage—From component to system level performance through dynamic modelling. Appl Energy 2017, 190: 84-98.

[4] Lei Chai, Jia Liu, Liang Wang, Lei Yue, Liang Yang, Yong Sheng, Haisheng Chen, Chunqing Tan. Cryogenic energy storage characteristics of a packed bed at different pressures. Appl. Therm. Eng. 2014, 63: 439-46.

[5] Yi Jin, Le Wang, Yuceng Yang, Jie Song, Chao Xu. Cycle performance of a packed bed based cold storage device. Energy Storage Science and Technology 2017, 6: 708-17.

[6] Lars Hüttermann, Roland Span. Influence of the heat capacity of the storage material on the efficiency of thermal regenerators in liquid air energy storage systems. Energy 2019, 174: 236-45.

[7] Hao Peng, Rui Li, Xiang Ling, Huihua Dong. Modeling on heat storage performance of compressed air in a packed bed system. Appl Energy 2015, 160: 1-9.

[8] Anton Meier, Christian Winkler, Daniel Wuillemin. Experiment for modelling high temperature rock bed storage. Sol. Energy Mater. 1991, 24: 255-64.

[9] Ran Li, Zhongwei Huang, Xiaoguang Wu, Pengsen Yan, Xianwei Dai. Cryogenic quenching of rock using liquid nitrogen as a coolant: Investigation of surface effects. Int. J. Heat Mass Transfer 2018, 119: 446-59.

[10] Zhirong Liao, Hua Zhong, Chao Xu, Xing Ju, Feng Ye, Xiaoze Du. Investigation of a packed bed
cold thermal storage in supercritical compressed air energy storage systems. Appl Energy 2020, 269: 115132.

Acknowledgement
This work was funded by the National Key R&D Program of China (No.2017YFB0903603) and Youth Science and Technology Innovation Project (CRYOQN202108) from the CAS Key Laboratory of Cryogenics, TIPC.