Performance Assessment of an Open Thermochemical Heat Storage (TCHS) System Using Composite Salt Hydrates

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Abstract. Heat storage performance of an open thermochemical heat storage (TCHS) system using composite salt hydrates of Wakkanai siliceous shale (WSS) - 9.6 wt.% LiCl was investigated numerically. A two-dimensional model considering the combined heat and mass transfer was developed. The calculation results were validated by the experimental results obtained in our previous study. The inlet air temperature, inlet air relative humidity, humid air flow rate, the ratio of the thickness of air channel and the thickness of composite solid wall, and length of the TCHS unit were evaluated to evaluate the heat storage performance. When the ratio of the thickness of air channel and the thickness of composite solid wall is 5 and the length of the heat storage unit is 0.1 m, the volumetric heat storage density of the open TCHS system can reach 510 MJ/m³.

1. Introduction

Thermochemical heat storage (TCHS) technology using salt hydrates is suitable to store low and medium temperature heat such as solar energy, because it has the advantages of suitable regeneration temperature, moderate reaction, high heat storage density, non-pollution, low heat loss and high-level safety [1-4]. Pure salt hydrates have shown high volumetric heat storage densities, but their deliquescence and sensitivity to heat source temperature affect the cycle stability strongly when they are used in open TCHS systems. Therefore, researchers have taken more attention on the research of the heat storage performance of composite salt hydrates in open TCHS systems. Kinds of composite salt hydrates have be developed by filling pure salt hydrates into pores of porous materials [5, 6].

WSS is a kind of natural mesoporous stone with SiO₂ as the main composition. The composite WSS - 9.6wt% LiCl has been obtained by impregnating LiCl into mesopores of WSS, which was made into a honeycomb structure. The heat storage performance of the honeycomb WSS - 9.6wt% LiCl was studied by experiments previously [7], which can be even regenerated at a low temperature of 60 °C with a volumetric heat storage density of 150 MJ/m³. However, kinds of parameters affecting the heat storage performance of the WSS - 9.6wt% LiCl have not been evaluated yet.

Therefore, a numerical study on the heat storage performance of the open TCHS system using WSS - 9.6wt% LiCl was conducted in this study. The temperature and humidity distribution of the WSS - 9.6wt% LiCl can be obtained to evaluate the heat storage performance of the TCHS system. The heat storage condition and the structure of the WSS - 9.6wt% LiCl can also be optimized in order to get a high volumetric heat storage density.
2. Description of the model of WSS - 9.6wt% LiCl
The structure of the honeycomb WSS - 9.6wt% LiCl is shown in Figure 1, whose physical properties of composite materials can be checked in Table 1 in our previous study [7]. In the open TCHS system using WSS - 9.6wt% LiCl, hot and dry air is pumped into the WSS - 9.6wt% LiCl composite honeycomb unit in the heat storage process, during which the bonded water vapor is discharged to the flowing hot air and the heat is stored. While in the heat release process, high humidity and low temperature air flows through the WSS - 9.6wt% LiCl composite honeycomb unit, and reverse process happens corresponding by releasing heat.

![Figure 1. Structure of WSS - 9.6wt% LiCl composite honeycomb unit [7].](image)

2.1 Model description
A two-dimensional transient model has been built as illustrated in Figure 2. It consists of two domains of the air channel and the composite solid side.

![Figure 2. Two-dimensional transient model.](image)

The mass conservation equation in the air channel is expressed in eq. (1).

\[
\frac{\partial}{\partial t} \rho_g u_g + \rho_g \nabla x_g = \rho_g \nabla \left( D_g \nabla x_g \right) + \frac{h_m}{d_g} (x_s - x_g)
\]

(1)

Where, \( \rho_g \) is the density of the air (kg/m³); \( u_g \) is the velocity of air (m/s); \( x_g \) and \( x_s \) are the absolute humidity of air in air channel and in composite solid side (g/kg DA); \( D_g \) is the diffusion coefficient of the air (m²/s); \( h_m \) is the convective mass transfer coefficient (m/s).

The energy conservation equation in the air channel is formulated as follows:

\[
\rho_g c_{pg} \frac{\partial T_g}{\partial t} + \rho_g c_{pg} u_g \cdot \nabla T_g = \nabla \cdot \left( \lambda_g \nabla T_g \right) + \frac{h}{d_g} (T_s - T_g)
\]

(2)

Where, \( T_g \) and \( T_s \) are the temperature of air and composite solid side (°C); \( c_{pg} \) and \( \lambda_g \) are the specific heat capacity (J/(kg K)) and the thermal conductivity (W/(m K)) of the air; \( h \) is the heat transfer coefficient (W/(m² K)).

The mass transport in the composite solid side is described as:
\[ \rho_s \epsilon \frac{\partial X}{\partial t} = \rho_s \nabla \cdot (D_{sd} \nabla X_s) - \rho_s \frac{\partial X}{\partial t} + \frac{h_m}{d_s} (x_g - x_s) \quad (3) \]

Where, \( \epsilon \) is the porosity of the composite WSS - 9.6wt% LiCl; \( X \) is the instantaneous sorption amount (gH_2O/gmaterial). Diffusion in porous composite material consists of molecular diffusion, Knudsen diffusion and surface diffusion, in which surface diffusion is generally the main transport mechanism in mesoporous materials [8, 9]. The surface diffusion coefficient \( D_{sd} \) is expressed by eq. (4) [10].

\[ D_{sd} = D_0 \exp \left(-\frac{E}{RT_s}\right) \quad (4) \]

Where, \( E \) is the activation energy (J/mol); \( D_0 \) is the exponential constant (m^2/s); \( R \) is the gas constant.

The energy conservation equation in the composite solid side is written as:

\[ \rho_s c_{ps, eff} \frac{\partial T_s}{\partial t} + \rho_s c_{ps} \frac{\partial T_s}{\partial t} = \nabla \cdot \left( \lambda_s \nabla T_s \right) + \rho_s H_s \frac{\partial X}{\partial t} + \frac{h}{d_s} (T_s - T) \quad (5) \]

Where, \( \rho_s \) is the apparent density of composite material (kg/m^3); \( H_s \) is the sorption heat of 2.26×10^6 J/kg. The effective specific heat capacity \( c_{ps, eff} \) and effective thermal conductivity \( \lambda_s \) are considered to be related to the sorption amount, which can be expressed by the following equations.

\[ c_{ps, eff} = c_{ps} + c_{H_2O} \cdot X \quad (6) \]

\[ \lambda_s = \lambda_s + \lambda_{H_2O} \cdot X \quad (7) \]

Where, \( c_{ps} \) is the specific heat capacity of the composite solid material (J/(kg K)), \( \lambda_s \) is the thermal conductivity of the composite solid material (W/(m K)). The Linear driving force mode (LDF) model [8] is adopted to predict the sorption rate of the WSS - 9.6wt% LiCl.

\[ \frac{dX}{dt} = \frac{K}{d_s} (X_{eq} - X) \quad (8) \]

Where, \( X_{eq} \) is equilibrium sorption amount (gH_2O/gmaterial), which has been tested at different temperatures and relative pressures; \( K \) is the total mass transfer coefficient (m/s), which is usually related to the diffusion coefficient of \( D_{sd} \) and can be defined by the following equation [8, 10].

\[ K = \frac{15D_{sd}}{d_s} \quad (9) \]

2.2 Initial and boundary conditions

2.2.1 Initial conditions The initial conditions for the air and the composite WSS - 9.6wt% LiCl in the heat storage process and heat release process are set as eq. (10) and (11), respectively.

\[ T_g = T_s = T_{g, release, final}, x_g = x_s = x_{g, release, final}, X = X_{release, final} \quad (10) \]

\[ T_g = T_s = T_{g, in, storage}, x_g = x_s = x_{g, storage, final}, X = X_{storage, final} \quad (11) \]

2.2.2 Boundary conditions Inlet air condition during heat release process:

\[ T_{g, in}(0, t_{release}) = T_{g, in, release}, x_{g, in}(0, t_{release}) = x_{g, in, release} \quad (12) \]

Inlet air condition during heat storage process:

\[ T_{g, in}(0, t_{storage}) = T_{g, in, storage}, x_{g, in}(0, t_{storage}) = x_{g, in, storage} \quad (13) \]

Wall boundary conditions: Zero flux is used as the wall boundary condition.

\[ \frac{\partial T}{\partial y} = 0, \quad \frac{\partial X}{\partial y} = 0, \quad y = d_s + d; \quad \frac{\partial T}{\partial y} = 0, \quad \frac{\partial X}{\partial y} = 0, \quad y = 0 \quad (14) \]
3. Results and discussion

Two performance indices of total heat output $Q_s$ and the volumetric heat storage density $q_v$ are defined as follows, which will be used to evaluate the heat storage performance of the TCHS system.

$$Q_s = \rho g C_p G \int_0^t (T_{g,\text{out}} - T_{g,\text{in}}) \, dt$$  \hspace{1cm} (15)

$$q_v = \rho g C_p G \frac{\int_0^t (T_{g,\text{out}} - T_{g,\text{in}}) \, dt}{V}$$  \hspace{1cm} (16)

3.1 Model validation

The finite element method is used for the calculation. Our previous experimental results of the open TCHS system using WSS - 9.6wt% LiCl [7] are used to verify the simulation results. As shown in Figure 3, the simulated outlet air temperature in heat release process is higher than that tested by experiment. Figure 4 shows that the calculated temperature of the measuring point near the outlet is higher than that obtained by experiment. The deviation of the outlet air temperature can be explained by the heat loss in the heat release process in experiment, which has been ignored in the simulation. The calculated outlet relative humidity predicts well the experimental value as shown in Figure 5.

![Figure 3. Comparison of inlet and outlet air temperatures in heat release process.](image)

![Figure 4. Comparison of measuring point temperatures in heat release process.](image)

![Figure 5. Outlet and inlet air relative humidities in heat release process.](image)

![Figure 6. Outlet and inlet air temperatures in heat storage process.](image)

Figure 6 and Figure 7 show that the simulated outlet air temperature and the temperatures at measuring points slightly lag behind the relevant experimental values in the heat storage process. The calculated outlet air relative humidity is slightly lower than that measured by the experiment. It is considered that the main reason of this deviation is the desorption rate is lower when the sorption amount is high, so perhaps the adopted LDF model cannot describe the desorption rate well.
3.2 Parametric studies

There are five parameters being evaluated, which are listed in Table 1.

Table 1 Simulated conditions.

| Parameter                                      | Value               |
|------------------------------------------------|---------------------|
| Ratio of thickness of air channel and composite solid wall, \( e \) (-) | 3, 4, 5, 6, 7       |
| Length of the unit, \( L \) (m)                | 0.1, 0.2, 0.3       |
| Inlet air temperature, \( T_{g,in,release} \) (°C) | 15, 20, 25, 30     |
| Inlet air relative humidity, \( RH_{in} \) (%) | 65, 75, 85, 95      |
| Humid air flow rate, \( G \) (m³/h)             | 2, 3, 4, 5, 6, 7    |

3.2.1 Effect of the ratio of the thickness of air channel and solid wall: \( e \)

In the simulation, the thickness of the composite solid wall remains 0.28 mm. The widths of the air channel are 0.84 mm, 1.12 mm, 1.4 mm, 1.68 mm and 1.96 mm with the \( e \) of 3, 4, 5, 6, and 7. Moreover, the mass ratio of water vapor in the air channel to the composite solid side are set to be constant during calculations.

The effects of \( e \) on the instantaneous outlet air relative humidity and outlet temperature are shown in Figure 9. The high outlet air temperature of lower \( e \) can last longer time. Moreover, it can be seen from Figure 10 that when \( e \) is 5, the volume heat storage density \( q_v \) and the total heat output \( Q_s \) are the highest. Therefore, the optimal ratio of thickness between the air channel and the composite solid wall is 5, which means that the thickness of composite solid wall is 0.28 mm and the width of the air channel is 1.4 mm.

3.2.2 Effect of the length of the TCHS unit: \( L \)

The effects of \( L \) on the instantaneous outlet air relative humidity and outlet air temperature are shown in Figure 11. The high outlet air temperature can last longer time if \( L \) is longer. It can be seen from Figure 12 that the total heat output \( Q_s \) increases with the rise of \( L \). However, when the \( L \) is 0.1, the volumetric heat storage density \( q_v \) is as high as 510 MJ/m³.
It can be explained that the water vapor content of the humid air gradually decreases along the air flow direction during the heat release process. If the TCHS unit is too long, the extra length cannot release relevant heat at a certain time because of relative low sorption amount of the extra length. Therefore, the volumetric heat storage density $q_v$ decreases with the $L$.

3.2.3 Effect of the inlet air temperature: $T_{g,in,release}$ The effects of $T_{g,in,release}$ on the instantaneous outlet air relative humidity and outlet air temperature are shown in Figure 13. The maximum temperature difference of the outlet air temperature and inlet air temperature grows with the increase of $T_{g,in,release}$. As shown in Figure 14, the TCHS system exhibits higher volumetric heat storage density $q_v$ and larger total heat output $Q_s$ when the inlet air temperature is set to be higher.

3.2.4 Effect of the inlet air relative humidity: $RH_{in}$ The effects of $RH_{in}$ on the instantaneous outlet air relative humidity and outlet air temperature are shown in Figure 15. Because the sorption amount of
the composite WSS increases as the relative humidity is raised, the outlet air temperature increases as the $RH_0$ is raised too, which indicates higher volumetric heat storage density $q_v$ and total heat output $Q_s$.

### 3.2.5 Effect of the humid air flow rate $G$

The effects of $G$ on the instantaneous outlet air relative humidity and outlet air temperature are shown in Figure 17. The humid air flow rate has important effect on duration of high outlet air temperature. Figure 18 shows that both the volumetric heat storage density $q_v$ and total heat output $Q_s$ increase as the humid air flow rate $G$ rises. Because the high outlet air temperature duration is shorten with the increase of $G$, the optimal $G$ should be calculated according to the actual application requirements about outlet air temperature.

![Figure 17. Effects of $G$ on the outlet air temperature and relative humidity.](image)

![Figure 18. Effects of $G$ on the $q_v$ and $Q_s$.](image)

### 4. Conclusion

In this study, heat storage performance of an open TCHS system using WSS - 9.6 wt.% LiCl was investigated numerically. (1) The developed model can predict the air temperature, relative humidity and the composite WSS - 9.6 wt.% LiCl’s temperature well. (2) The optimum $e$ is 5 to get a high volumetric heat storage density and high heat output. (3) The volume heat storage density decreases with the increase of the length of the TCHS unit. (4) Both the volume heat storage density and total heat output increase as the inlet air temperature and the inlet air relative humidity. (5) The volumetric heat storage density and total heat output increase with the rise of the inlet air flow rate.

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