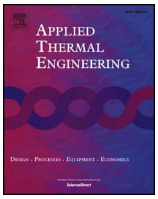
Applied Thermal Engineering 135 (2018) 95–108

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng



Research Paper

Analysis of thermal deposition of $MgCl_2·6H_2O$ hydrated salt in the sieve-plate reactor for heat storage

Wei Chen, Wei Li*, Yunsong Zhang

School of Merchant Marine, Shanghai Maritime University, Shanghai 201306, PR China

HIGHLIGHTS

- A novel reactor model is proposed to improve the heat and mass transfer effect for heat storage system.
- The structural parameters of the reaction bed are optimized.
- The energy storage process under different operating conditions is analyzed.

ARTICLE INFO

Keywords:
$MgCl_2·6H_2O$ hydrous salt
Dehydration
Thermochemical energy storage
Heat and mass transfer
Numerical analysis

ABSTRACT

Hydrated salt thermochemical energy storage which utilizes reversible gas–solid reactions to store heat for charging and release heat for discharging has a promising application in the energy utilization system. A novel sieve-plate hydrated salt thermochemical energy storage system (TCES) with the reactive porous bed of $MgCl_2·6H_2O$ is investigated, and the mathematical equations describing the heat and mass transfer for the TCES are developed to analyze the effects of the geometric parameters of reactor and operating conditions on the thermal decomposition of $MgCl_2·6H_2O$ salt during charging (dehydration). The rises of the sieve plate number and length within a certain degree cause the shorten time to reach the equilibrium extent conversion at input temperature. The δ, ratio of channel width h_1 to reactive bed thickness $h_{0,}$ needs to be optimized to achieve higher dehydration efficiency. More residence time of heating gas and more heat storage can be achieved with the relatively higher input temperature. The kinetic factor needs to be above $R_{kin} = 1 \cdot 10^{-3}\,s^{-1}$ to avoid lower extent conversion and larger time length for the reactive bed to reach the equilibrium phase at input temperature. The dehydration efficiency in the reactive bed and the heat utilization rate of heating gas in the charging are related to the heating gas velocity. The simulations agree with the published TGA-DSC testing results. For the current mode, the reactor with a 6 sieve plates of $L_0 = 24–26\,cm$ and a $\delta = 0.8$ flow channel as well as the relatively higher thermal conductivity and operating temperature within a certain degree in the reactive bed are proposed.

1. Introduction

As the energy crisis is getting worse, renewable energy has been widely put into utilization. The long-term and cross-space energy storage serves as a promising method to obtain higher energy efficiency and generate a larger scale of renewable source, thus it has attracted many researchers' attentions [1–4]. Compared with sensible heat storage and latent heat storage, thermochemical heat storage (THS) exhibits a higher energy storage density (about 200–500 $kWh\,m^{-3}$) [5] and smaller heat losses during storage due to the energy stored in chemical potential [2,4], thus, THS can be used as a cross-seasonal energy storage [1,6–9]. In general, there are two types of THS according to the thermochemical reaction without sorption or with chemisorption [10]. In the THS without sorption that is also considered as chemical storage systems, a reversible exothermic synthesis reaction takes place among two or more separate chemical substances, where large amount of energy is stored or generated, but the operation is very demanding and reaction process is complicated as well as other by-product may be produced, such as the oxide/hydroxide reversible reactions of $CaO/Ca(OH)_2$ and $MgO/Mg(OH)_2$ [11,12], metal/metal hydride reaction of Mg/MgH_2 [13], metal/metal hydride reaction of $CaO/CaCO_3$ [14], redox chemical reaction of CoO/Co_3O_4 [15], CO_2 reforming of methane reaction[16], and ammonium hydrogen sulfate chemical reaction [17]. In the THS with chemisorption, a relatively

---

* Corresponding author.
E-mail addresses: weichen@shmtu.edu.cn (W. Chen), limingwei93@163.com (W. Li), kyyxstg@126.com (Y. Zhang).

https://doi.org/10.1016/j.applthermaleng.2018.02.043
Received 25 August 2017; Received in revised form 11 February 2018; Accepted 13 February 2018

Nomenclature

A_f	frequency factor, 1/s
C_0	initial concentration of salt-hydrate, mol/m^3
C_f	final concentration of the salt-hydrate, mol/m^3
C_p	specific heat, J·kg^{-1}·K^{-1}
C(t)	concentration of the salt-hydrate at a given time, mol/m^3
D_g	effective gas diffusivity in porous reactive bed, m^2/s
E_a	Arrhenius activation energy, J/mol
$E_{a,w}$	activation energy for desorption, J/mol
g	acceleration of the gravity, m^2/s
h_1	width of flow channel, cm
h	thickness, cm
h_0	thickness of reactive bed, cm
H	height, cm
ΔH_r	enthalpy of reaction, kJ/mol
L	width, cm
L_0	length of sieve plate, cm
m_0	initial mass of salt-hydrate, g
m_{v0}	initial water vapor content in heating air at the inlet, g
m_f	final mass salt-hydrate, g
m(t)	mass of salt-hydrate at a given time, g
m_{v0}	water vapor content in the outlet heating air at a given time, g
m_{sat}	water vapor content of saturation in heating air at input temperature, g
N	number of reactive bed in the reactor
p	pressure, Pa
p_v	water vapor pressure, Pa
p_{eq}	equilibrium pressure, Pa
R	ideal gas constant, J/mol/K
R_{kin}	kinetic factor, 1/s
ΔS	entropy of the reaction of dehydration, J/mol/K
t	time (s)
T	temperature, K or °C
T_p	peak temperature usually obtained in thermal analysis experiment, K or °C
T_{eq}	equilibrium temperature, K or °C
T_v	gas phase temperature at the critical point on equilibrium curve, K or °C
T_s	solid phase temperature at the critical point on equilibrium curve, K or °C
u	velocity component in x-direction, m/s
u_{fd}	internal gas velocity during desorption, m/s
u_{in}, u_0	inlet velocity of hot fluid, m/s
v	velocity component in y-direction, m/s

Greek symbols

α	extent conversion or conversion degree, %
β	heating rate, K min^{-1}
μ	viscosity, Pa s
γ	thermal expansion coefficient, 1/K
ε	void fraction or porosity of the material bed
λ_s	thermal conductivity of material in solid phase, W/m K
λ_g	thermal conductivity of gas, W/m K
φ	Relative humidity, $\varphi = \frac{p_v}{p_s}$, %
z	stoichiometric coefficient of water
ρ	density, kg m^{-3}
δ	the ratio of channel width to reactive bed thickness
η	relative rise ratio
dα/dt	reaction rate, 1/s

Subscripts

0	initial condition
eff	effective
eq	equilibrium state
f	final state
fd	Darcy flow
g	gas phase
kin	kinetic
in	inlet
v	vapor
s	solid
r	reaction
ref	reference

small amount of energy with a lower temperature can cause the reaction of thermochemical heat storage due to its lower activation energy requirement, which makes the THS with chemisorption more feasible for low temperature utilizations than that without sorption [18], such as the dehydration and hydration of inorganic hydrates (hydrous salt pairs), metal hydrides, ammoniated pairs. In this paper, TCES systems of hydrous salt utilizing reversible gas–solid reactions to store or release heat during charging (dehydration) or discharging (hydration). The dehydration and hydration chemical reaction of inorganic salt can be expressed as follow:

$$Salt{\cdot}x\mathrm{H_2O_{(s)}} + \Delta H \Leftrightarrow Salt{\cdot}(x-y)\mathrm{H_2O_{(s)}} + y\mathrm{H_2O_{(g)}} \quad (1)$$

In the charging (dehydration) process, hydrous salt is heated to be in a less hydrous or anhydrous state by the input heating gas due to the occurrence of reversible gas–solid reactions, thus heat is stored in the salt bed in chemical potential energy; the hydration process serves as discharging phase to supply heat for use when the water vapor is input for the salt hydration during discharging [19,20], shown in Fig. 1.

So far, inorganic hydrate salts have proven to be reliable in developing thermal energy storage systems for building applications and heat recovery [1,9,21,22]. Combining a thermochemical heat storage unit of inorganic hydrous salt to a home-device micro cogeneration of heat and power (micro-CHP) was proposed to improve the efficiency of energy utilization [18,21,23–25]. The requirements of high energy storage density, non-toxic, stable performance, high recyclability and cheaper price or easy to prepare need to be met while the inorganic hydrous salts are used for energy storage and release rationally and effectively: Wang et al. [26] summed up the common adsorption/absorption heat storage methods and the corresponding materials. Kubota et al. [27] analyzed and evaluated the chemical reactions of hydrated salt. It has been shown that the better properties of heat storage and more than 1000 kJ/kg energy storage density can be obtained for the crystalline

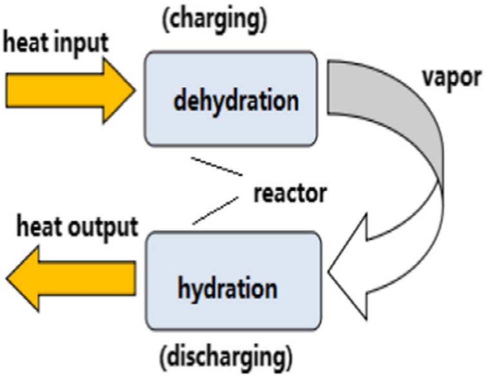


Fig. 1. Schematic principle of TCES based on hydrated salts.