International Journal of Heat and Mass Transfer 54 (2011) 4856–4863

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

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

Release of stored thermochemical energy from dehydrated salts

Mehdi Ghommem [a], Ganesh Balasubramanian [a], Muhammad R. Hajj [a], William P. Wong [b], Jennifer A. Tomlin [c], Ishwar K. Puri [a,*]

[a] Department of Engineering Science and Mechanics, Virginia Tech, Blacksburg, VA 24061, USA
[b] Science Applications International Corporation, Ottawa, ON, Canada K1P 5Y7
[c] Science Applications International Corporation, Blacksburg, VA 24060, USA

ARTICLE INFO

Article history:
Received 2 May 2011
Received in revised form 23 June 2011
Accepted 23 June 2011
Available online 27 July 2011

Keywords:
Thermochemical reaction
Energy storage
Salt hydrates
Sensitivity analysis
Polynomial chaos expansion

ABSTRACT

Thermochemical materials, particularly salt hydrates, have significant potential for use in thermal energy storage applications. When a salt hydrate is heated to a threshold temperature, a chemical reaction is initiated to dissociate it into its anhydrous form and water vapor. The anhydrous salt stores the sensible energy that was supplied for dehydration, which can be later extracted by allowing cooler water or water vapor to flow through the salt, transforming the stored energy into sensible heat. We model the heat release that occurs during a thermochemical hydration reaction using relations for mass and energy conservation, and for chemical kinetics and stoichiometry. A set of physically significant dimensionless parameters reduces the number of design variables. Through a robust sensitivity analysis, we identify those parameters from this group that more significantly influence the performance of the heat release process, namely a modified Damköhler number, the thermochemical heat capacity, and the heat flux and flowrate. There is a strong nonlinear relationship between these parameters and the process efficiency. The optimization of the efficiency with respect to the parameters provides guidance for designing engineering solutions in terms of material selection and system properties.

1. Introduction

Long-term energy storage and release can be facilitated by the use of salt hydrates [1]. Upon heating, these materials release the water coordinated to the solid crystal through a thermochemical reaction. This results in an anhydrous form of the salt that also chemically stores the energy supplied for the thermochemical reaction. Anhydrous salts are typically hygroscopic and thus able to absorb or adsorb atmospheric water vapor even at room temperatures [2]. The reverse mechanism of salt hydration releases the stored energy. Although recrystallization and nucleation effects during hydration raise important questions about their durable cyclical use over time, thermochemical salt hydrates have several advantages over phase change materials [3–5] and latent heat storage devices [6,7] for long-term energy storage [8], transportation and release [9,10]. For instance, salt hydrates exposed to solar energy during summer months will result in the corresponding dehydrated salts and water vapor. These products can be separately stored until the winter when they can be recombined through salt hydration to release the stored heat. This process, which can be used to warm buildings, has been demonstrated for centralized solar seasonal energy storage [3,11–13].

We have previously described the fundamentals associated with the energy storage in a salt hydrate [1]. Here, we provide a similar analysis of the reverse heat release process from these salts. Since the performance of the thermal storage and release can be significantly improved by exploiting specific material behaviors, our analysis provides additional information by which to evaluate the impact of various system parameters on the recovery of the thermochemically stored energy. Unlike a typical parametric analysis based on the classical sweep approach that requires several simulations, we use uncertainty quantification tools [14–16] that provide a robust sensitivity analysis [17,18]. Thus, we are able to quantitatively determine the role of the key thermodynamic process parameters [1] that influence the performance of thermochemical storage-release systems. Magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$) is chosen as the model salt due to its large volumetric energy storage capability [19]. (The words 'anhydrous' and 'dehydrated' are used interchangeably hereafter.)

2. Modeling the energy release process

Experiments designed to measure the thermochemical energy release process comprise of an insulated container filled with the dehydrated salt. Cooler water vapor in excess of that required for

* Corresponding author. Address: 223A Norris Hall (MC 0219), Blacksburg, VA 24061, USA. Tel.: +1 540 231 3243; fax: +1 540 231 4574.
E-mail address: ikpuri@vt.edu (I.K. Puri).

0017-9310/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijheatmasstransfer.2011.06.041

Nomenclature

A	frequency factor in Arrhenius' equation (s^{-1})
C	specific heat capacity (J/kg K)
D_m	modified Damköhler number
E	activation energy in Arrhenius' equation (kJ/mol)
ΔH	enthalpy of hydration (J/kg)
K	thermal conductivity (W/m K)
L	length of the simulation domain (m)
M	molar mass (gm/mol)
N	concentration (mol/m^3)
Q	energy released per unit volume (J/m^3)
R	Universal gas constant (J/(K mol))
T	temperature (K)
$\mathbf{n}$	unit normal vector
q	heat flux (W/m)
n	number of random variables
p	order of the polynomial chaos
r	rate of reaction (s^{-1})
t	time (s)

Greek symbols

Γ	simulation domain boundary
Π	process efficiency
α^*	generic variable
β	mass fraction
γ	rate of water vapor supplied to the anhydrous salt (s^{-1})
η	dimensionless heat capacity per unit volume
ρ	density (kg/m^3)
χ	dimensionless thermochemical heat capacity
ζ	number of moles
λ	uncertain parameter
μ	mean value
σ	standard deviation
ξ	random variable

Subscripts

d	dimensional parameter
e	end of overall heat transfer process
h	salt hydrate
g	water vapor
r	initiation of thermochemical reaction
r, e	end of thermochemical reaction
s	anhydrous salt
x	axis along the horizontal direction
y	axis along the vertical direction

complete hydration is passed over the salt. On coordination with water, the anhydrous salt converts to the hydrated form, simultaneously releasing energy that warms the excess water vapor flowing over the hydrated salt [12,13]. We, instead, employ an imposed heat flux that is extracted continuously from our model system as an analogy to the energy carried out by the warmer water vapor in the experiments. While our model system is simple and constructed to understand the fundamentals of the process, the study of a detailed geometric configuration to mimic the experiment is one of our future goals.

Fig. 1 contains a schematic of the simulation configuration. We consider a square $L_x \times L_y$ two-dimensional box ($L_x = L_y = L = 0.01$ m) that is filled with the dehydrated $MgSO_4$. This anhydrous salt, which has a higher internal energy than its hydrated counterpart due to the thermochemical energy stored in it, is also at a higher temperature than its surroundings that are at room temperature. Thermal energy is extracted from the system at a constant rate q_d from its right boundary. The enclosing walls on the top, left and bottom, shown in Fig. 1, are insulated and considered adiabatic.

The thermochemical process is initiated when the local temperature *decreases* to the reaction temperature $T_r = 473$ K. This threshold triggers the interaction (hydration) of the anhydrous salt with the cooler water vapor that is introduced into the system. Dehydrated salts are porous media. As an increasing fraction of the porous volume is filled by the supplied water vapor, we assume that the rate of vapor flow into the system decreases, since there is now a greater resistance to the vapor inflow as well as relatively less void spaces for the water molecules to diffuse into. Therefore, we introduce water vapor into the system using a time dependent function $N_g = N_{g,i}(\arctan(\gamma_d t)/(\pi/2))$ until all the vacant spaces in the porous medium are filled. Here, $N_{g,i}$ denotes the concentration

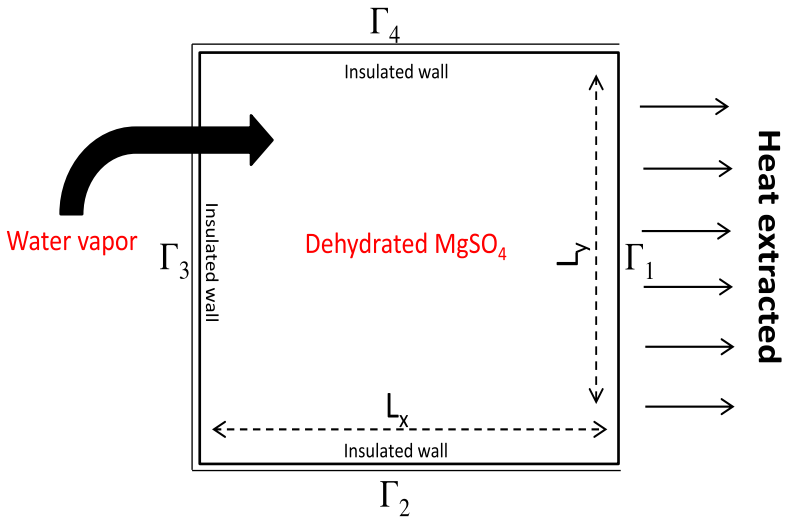

Fig. 1. Schematic of the heat release process.