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Salt impregnated desiccant matrices for 'open' thermochemical energy storage—Hygrothermal cyclic behaviour and energetic analysis by physical experimentation

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ABSTRACT

A selection of hygroscopic salts and desiccant matrices (Salt In Matrix, SIM) were chosen from the part I of this research through characterisation of their pore structure and hygrothermal functional properties as candidate materials for a novel open thermal energy storage (TES) system. The aim of the paper was to analyse the candidate materials performance under controlled, large scale experimental tests. This was achieved through hygrothermal cyclic behaviour tests and energy and exergy analysis.

Zeolite provided the highest temperature lift of all candidates due to the high amount of vapour adsorption and its fast reaction kinetics however, after the initial period (1–2 h), the moisture adsorption rate and thus heat generation decrease sharply. Zeolite also showed a sharp drop in performance over the four cycles as it requires a higher regeneration temperature (>180 °C) than that used (100 °C) for this research. SIM-3a (Vermiculite–$CaCl_2$) was found to be the most promising candidate for open TES systems due to its high heat generated and rapid mass uptake at higher relative humidity levels.

1. Introduction

There are many sources of renewable energy that are both well researched and widely utilised in the domestic sector to provide heat and electricity. These include biomass boilers [1], geothermal heat pumps [2], wind turbines [3], solar photovoltaic units [4] & solar thermal units such as flat plate collectors [4] and evacuated tubes [5]. Whilst these technologies are theoretically inexhaustible and abundant, there is often a large barrier to their successful implementation, namely a mismatch between the production of and demand for the energy they generate [6]. The total amount of solar heat gain with correctly orientated 10 m^2 flat plate solar collectors in the UK is 14,621 kW h which exceeds the typical energy consumption of an insulated building over the course of a year (13,899 kW h). Under UK climactic conditions, high energy generation/low demand occurs during the summer months whilst low generation/high demand occurs during winter. Successful, demand driven implementation of 'thermal' renewable technologies requires an inter-seasonal storage approach to address this mismatch.

There are many candidate systems that are currently used to provide domestic thermal energy storage (TES) such as electrical storage heaters, hot water tanks, highly insulated building envelopes coupled with thermal mass [7–11] and phase change materials (PCM) [7,12]. These systems, whilst being at an advanced state of research, are primarily designed to cope with diurnal energy demand only. Recently, an alternative option for inter-seasonal TES has emerged using salts entrapped within porous desiccant materials (*i.e.* Salt In Matrix—SIM) [13–15]. These systems utilise reversible thermochemical reactions to effectively store solar energy which can later be released as heat.

Thermochemical heat storage (THS) systems utilise one of two approaches; 'closed' or 'open' systems. 'Closed' systems are, in general, capable of providing much greater reaction efficiencies when compared to 'open' systems due to the lower reaction chamber pressures (sometimes vacuum) allowing increased vapour diffusion of the sorbate (gas) to the sorbent (SIM) [16]. 'Open' systems work under standard atmospheric pressures, negating the need for complex pressure systems however, there is much lower reaction efficiency due to a decreasing trend in diffusion causing instability during heat generation [17].

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Nomenclature

c_p	specific heat at constant pressure J/(kg K)
E_d	energy density (kJ/kg)
E_{cum}	cumulative thermal energy (kW h)
EMC	equilibrium moisture content (kg/kg)
Ex	exergy (kW)
H	enthalpy (kJ/s)
m	mass (g, kg)
ma	mass flow rate of air (kg/s)
P	pressure (Pa)
Q	energy (kW)
RH	relative humidity (%)
S	entropy (kJ/kg)
t_{emc}	time interval to reach EMC (h)
t	time (s, h)
T	temperature (°C, K)
V	volume (m^3)
ξ_A	moisture storage function where $\xi = f(RH_{ie})$ (kg/kg)
ξ_B	moisture storage function where $\xi = f(RH_{ie}, t_{emc})$ (kg/kg)
ρ	density (kg/m^3)
η_I	1st law efficiency (–)
η_{II}	2nd law efficiency (–)

Subscripts

tr	transferred
dr	discharging
cr	charging
g	gain
cum	cumulative
ads	adsorbent
a	air
wv	water vapour
w	wet
i	inlet
d	dry
ave	average
f	fan
h	heating
rxn	reaction

Fig. 1 shows the basic operating principle of an 'open' adsorption heat storage system with the flow numbers used in the later numerical analysis. During the discharging process, cold air is blown into the system with a mechanical fan. If required (*i.e.* in the case where inlet relative humidity, RH_{in} is low), moisture is added via a humidification unit. The cold and humid air (1) enters the reactor. The moisture is absorbed and heat generated due to the exothermic nature of the reaction. This releases hot and dry outlet air (2) which can be used for either space heating or water heating applications. In the reverse, during the charging process, hot and dry air (3) is heated before entering reactor. The absorbed moisture in the material is desorbed releasing cooler, humid air. Whilst there are advantages and disadvantages evident for both systems, the 'open' type system was adopted for this research due their simpler process design (*i.e.* no heat exchangers or pressure vessels) which in turn should allow for more straight forward operational conditions.

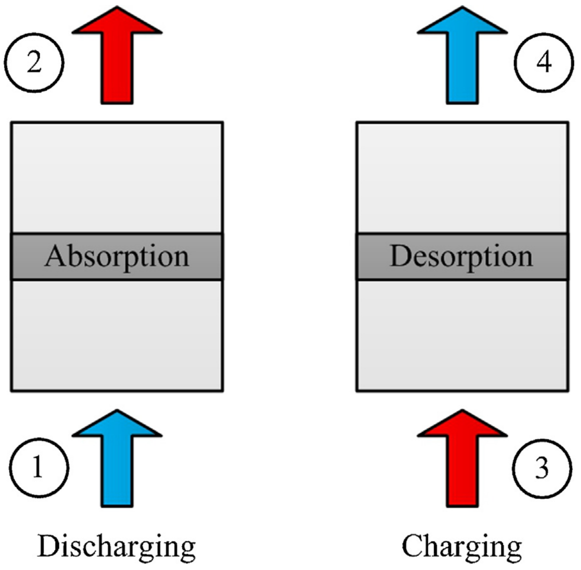

Fig. 1. Basic principle of 'open' adsorption heat storage.

In previous work by the authors [18] the pore geometry and hygrothermal properties of eight SIM materials and four host matrices were analysed to provide the specific properties based solely on material characterisation. Whilst characterisation is vital in providing insight into SIM behaviour, it is also necessary to analyse a materials performance under controlled, larger scale experimental tests. As discussed in the literature [19], a complete research approach is ideally based across the full scale of material behaviour however, due to time, financial and access limitations this is not always possible. The minimum four stages required to provide a complete 'map' of material behaviour are:

Stage 1 Investigations at the material level (i.e. characterisation of the hygrothermal properties and pore geometry)

Stage 2 Experimental investigations using scaled physical models (i.e. laboratory representations of 'ideal' conditions)

Stage 3 Numerical investigations using transient heat and moisture (HAM) models.

Stage 4 Full scale field testing (i.e. monitoring of psychrometric conditions and material behaviour in situ)

The aim of this paper is to perform hygrothermal cyclic behaviour tests using physical experimentation to address 'Stage 2' as outlined above on a selection of SIM samples and, to analyse these results, carry out energy and exergy analysis.

2. Candidate material selection, synthesis and characterisation

As stated, a recent trend has emerged using salts entrapped within porous desiccant materials to provide thermochemical TES. A review of both the current and past literature (see: [18] for more information) identified a number of candidate materials including activated carbon, vermiculite, silica gel, and synthetic zeolites as host matrices. Calcium Chloride ($CaCl_2$), Calcium Nitrate ($Ca(NO_3)_2$), Magnesium Sulphate ($MgSO_4$), Lithium Nitrate ($LiNO_3$) and Lithium Bromide (LiBr) were identified as suitable salts for entrapment. A number of these pairs were selected for testing to provide a cross-sectional representation of the full sample range (see: Table 1). Testing was also undertaken on the four raw matrix materials.

Table 1
Designation of SIM's with selected samples analysed highlighted in grey.

	Impregnated Salt				
	$CaCl_2$	$MgSO_4$	$Ca(NO_3)_2$	$Li(NO_3)_2$	LiBr
Silica Gel	SIM-2a	SIM-2b	SIM-2c	SIM-2d	SIM-2e
Vermiculite	SIM-3a	SIM-3b	SIM-3c	SIM-3d	SIM-3e
Activated Carbon	SIM-4a	SIM-4b	SIM-4c	SIM-4d	SIM-4e
Zeolite 13X	SIM-8a	SIM-8b	SIM-8c	SIM-8d	SIM-8e