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Salt impregnated desiccant matrices for 'open' thermochemical energy storage—Selection, synthesis and characterisation of candidate materials

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ABSTRACT

A selection of hygroscopic salts and desiccant matrices (salt in matrix, SIM) were chosen from the literature as candidate materials for open thermal energy storage (TES) systems. The aim of the paper was to narrow this selection through the application of selective criteria to those that had a high affinity of each working pair to each other, were environmentally stable, had low raw material costs with high availability, a low regeneration temperature for charging (<130 °C), a high temperature lift during reaction, high cyclic efficiency and high energy density. Candidate materials included silica gel, zeolite, activated carbon and vermiculite as matrices with $CaCl_2$, $MgSO_4$, $Ca(NO_3)_2$, $LiNO_3$ and LiBr as salts. Scanning electron microscopy was used to verify salt presence. The pore geometry and structure was mapped through the use of nitrogen (N_2) physisorption with application of both Brunauer–Emmett–Teller and Barrett–Joyner–Halenda analysis, gas pycnometry and gravimetric testing. The hygrothermal properties were characterised using modified transient plane source, differential scanning calorimetry and modified dynamic vapour sorption (DVS) techniques. Vermiculite with either lithium bromide (SIM-3e) or calcium chloride (SIM-3a) appear to have significantly higher TES potential when compared to both the raw desiccants and the other SIM's.

1. Introduction

According to a 2013 report, 45% of total UK final energy consumption for 2012 was for heating purposes, of which domestic usage accounted for 54% whilst the service sector and industry accounted for 19% and 27%, respectively [1]. Current production of this energy (domestic only) is spread primarily between Solid Fuel and Oil (12%), Natural Gas (78%) and Electricity (7%) whilst renewables (and others) account for 2% [2]. The decline in fossil fuel availability [3] coupled with the increasing price for those fuels [4] have led to increased focus in recent years on alternative and renewable sources of energy.

Whilst there are many forms of renewable energy available (wind, solar PV and thermal, wave, geothermal) which are potentially inexhaustible and abundant, there is often a large barrier to their successful implementation due to demand availability *i.e.* a mismatch between the production of and demand for that energy [5]. In total energy terms, the amount of solar radiation incident on a correctly orientated roof of a typical home in the UK exceeds its energy consumption over the course of a year [6]. During the summer months there is an excess of solar heat energy available (see: Fig. 1); however, there is little or no building heat demand due to occupant comfort conditions already being met or exceeded. Conversely, peak building heat demand occurs during the winter months due to lower external temperatures when production of solar energy is at its minimum. Most UK homes and businesses have systems in place to cope with diurnal energy offsets such as electrical storage heaters, hot water tanks, phase change materials (PCM's) [7], highly insulated building envelopes coupled with thermal mass [8], however there are currently few measures available for inter-seasonal thermal energy storage (TES).

There are many options available (see: Fig. 2) that have potential to provide acceptable inter-seasonal TES such as the thermochemical adsorption systems utilising desiccant storage materials such as zeolites [9–15], silica gels [14,16,17] and activated carbons [18–20]. There are also physical processes available based on both sensible heat *i.e.* solids and liquids [21–24] and latent heat technologies

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Nomenclature

c_p	*specific* heat at constant pressure (J/(kg K))
E_d	energy density (kJ/kg)
m	mass (g, kg)
kn	bulk porosity (m^3/m^3)
P	pressure (Pa)
RH	relative humidity (%)
RH_{ie}	interior environment relative humidity (%)
t_{emc}	time interval to reach equilibrium moisture content (h)
t	time (s, h)
T	temperature (°C)
w	specific moisture content (kg/kg)
w_0	specific moisture content in the dry state (kg/kg)
w_{95}	specific moisture content at RH = 95% (kg/kg)
V	volume (m^3)
λ	dry state thermal conductivity (W/(m K))
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)
ϕ	diameter (m)

involving materials that undergo a phase change *i.e.* solid → liquid, solid → gas [25–28]. Thermochemical systems perhaps offer the best opportunity in terms of inter-seasonal TES due to the completely reversible reactions that occur, however there are process limitations on their effectiveness such as the amount of material required, the heat of reaction of the material and thermodynamic operation of the complete system.

As stated, thermochemical TES systems utilise reversible reactions (chemical or sorption) to store and release heat. For example, in the summer solar heat energy is used to remove an absorbed gas (V) from a host material (M) in an endothermic reaction. The material is then stored hermetically until the winter when the gas is allowed to react with the material creating an exothermic reaction, releasing heat as described in Fig. 3. As such, no heat energy is stored inter-seasonally and therefore there are no losses due to

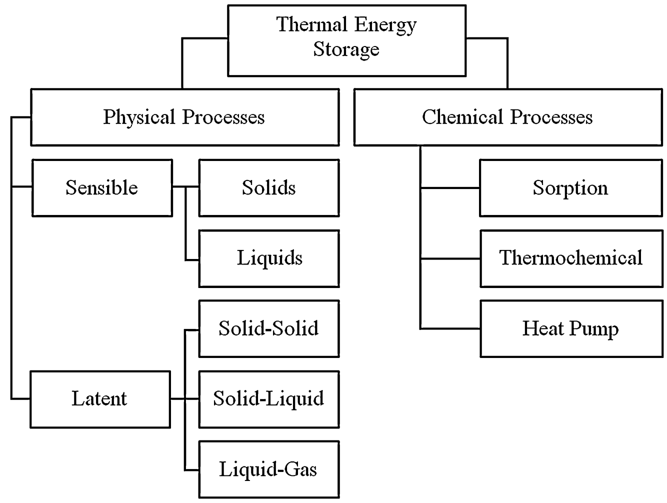

Fig. 2. Thermal energy storage methods. Adapted from [23].

heat degradation. The aim of this research is to select materials suitable for use as thermochemical heat storage mediums, specifically in 'open' systems for use under standard temperature and pressure (STP) conditions with water vapour as the adsorbate gas. Use of 'open' systems negates the requirement for both high vacuum setups and heat exchangers used in 'closed' systems. This required synthesis of sample materials and the complete characterisation of both their hygrothermal properties and pore structure in order to accurately correlate material type and behaviour.

2. Candidate material selection and synthesis

Similarly to the range of technologies presented in the TES reviews, there are many materials available for use in TES systems, dependent on system type. These can be categorised by heat storage mechanism; sensible, latent, adsorption, absorption and chemical reaction. Fig. 4 maps a small range of materials suitable for TES (among other applications). Reading from left to right, the storage potential or energy density, E_d, defined as the amount of energy accumulated per unit volume or mass [29] increases due to the

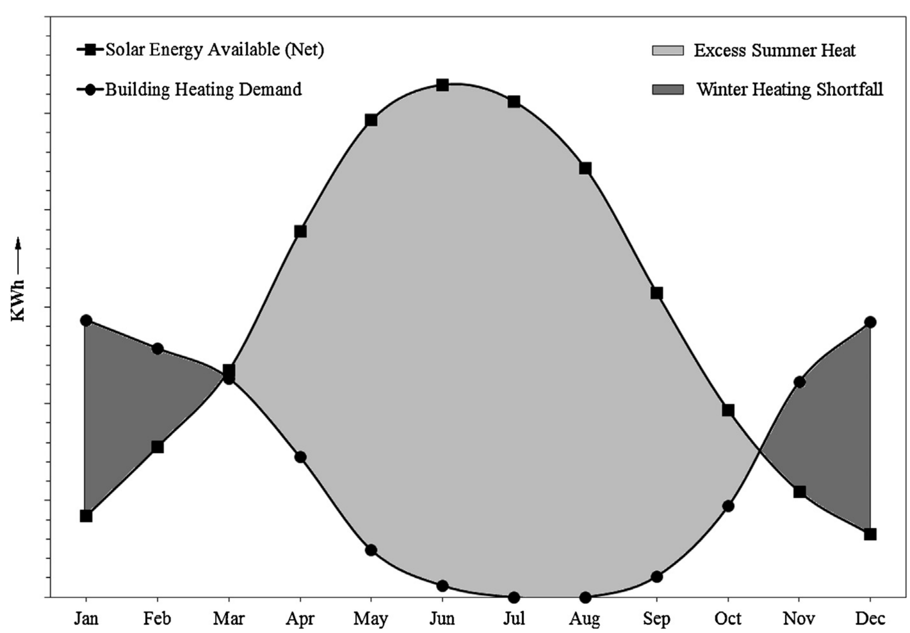

Fig. 1. Graph showing the mismatch between available solar energy and building heating demand.