



Humidity dependence of transport properties of composite materials used for thermochemical heat storage and thermal transformer appliances



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ABSTRACT

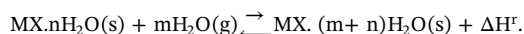
Water sorption thermochemical heat storage is a promising way to provide dwellings with renewable central heating. It requires the use of several cubic meters of materials per dwelling. Depending on the design of the heating system, specific heat and mass transfer issues occur. For instance, the heat transfer rate in reactive medium and the kinetics of sorption process determine the system thermal power. In addition, the moisture propagation during inter-seasonal storage must be understood. In this paper, the influence of the water mass uptake on the apparent thermal conductivity and apparent mass diffusivity of solid material were studied. The studied material was a composite of calcium chloride (CaCl₂) encapsulated in mesoporous silica with a salt content of 40–43 wt.%. The thermal conductivity was measured by the transient hot bridge method and varied from 0.13 to 0.16 W m⁻¹ K⁻¹, having a threshold at 0.14 g/g of water mass uptake. The apparent water mass diffusivity was studied using a diffusion column. The water diffusivity – concentration dependency was established by using the modified Hall method. The apparent diffusion coefficient ranged from 3 × 10⁻¹⁰ to 2 × 10⁻⁸ m² s⁻¹ in experimental conditions.

1. Introduction

Over the last twenty years, the research on thermochemical materials presented an important interest for thermal energy storage and heat transforming processes used by applications such as (i) residential heating and (ii) industrial waste heat recovery/heat upgrade. These applications aim at mitigating not only the environmental impact of the energy feedstock, but also the energy cost and efficiency of advanced economies. The design and integration of thermochemical appliances to the building sector strictly require their compactness. The size restriction condition is crucial which implies boosting the energy storage density (kW h stored per m³) of the thermochemical storage material, as well as its specific thermal power (W per m³). These parameters depend on the involved type of chemical bonds and kinetic characteristics.

Regarding the energy storage density, the best candidates can be found among salt hydrates. Some studies dealt with water sorption in saline conditions, where the enthalpy of dissolution is used to generate the heat [1,2]. Other works dealt with salts in solid form, like SrBr₂

[3–5], MgSO₄ [6] and CaCl₂ [7]. In this case, the formation of the various hydrates in the presence of water vapor results in the heat release, which can be used for the heat storage purposes:



Where MX signifies salt; m and n are integer numbers and ΔH^r is the reaction enthalpy. This process refers to the thermal energy storage and heat transforming by the mean of solid-gas thermochemical reversible reactions. It can be extended to other sorbents like alcohols or ammonia [8,9].

The specific thermal power depends on heat and mass transfer parameters.

The mass transfer parameters are directly affected for salts hydrates by the following phenomena:

- (i) Due to the crystallization of the various hydrates, the salt morphology is altered at each cycle, reducing their reversibility properties, causing the reduction of the heat amount that can be stored/

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released under real operating conditions [7].

- (ii) Many metal halides, e.g. CaCl_2 , LiCl , MgCl_2 , ZnCl_2 etc., are very soluble in water and are even able to dissolve in their own water of crystallization: this phenomenon is known as deliquescence [7,10–12]. This leads to the salt particles agglomeration into hard blocks during the dehydration process, which limits the exchange of water molecules.

An efficient way to overcome the mentioned drawbacks is to synthesize composite materials by incorporating the hygroscopic salt into a porous solid matrix that durably maintains microscopic pathways for the water vapor penetration or release. Molecular sieves such as zeolites [13,14], metal-organic frameworks [15], carbonaceous supports such as activated carbon [16] or expanded graphite [3], as well as siliceous supports (including mesoporous silica gel) [17,18] and carbon nanotubes [8,9,19,20], have been proposed as matrices for the composite materials synthesis. Generally, the porous matrix marginally participates to the sorption process, which is mainly due to the hydration/dehydration reactions of the salt. However, the thermodynamic properties of the encapsulated salt are different from those of the bulk salt. The early proposed composite material was synthesized by Aristov et al. using CaCl_2 trapped in silica gel [17].

The heat transfer parameters can be somewhat improved as well to boost the specific power at the macro-scale, by the use of highly heat conductive additives with the material [3,21]. For instance, the thermal conductivity of silica gel was increased from $0.106 \text{ W m}^{-1} \text{ K}^{-1}$ to $0.363 \text{ W m}^{-1} \text{ K}^{-1}$ by adding aluminium scraps [21]. However, this way results in the drop of the material energy storage density, because the heat conductive additive is inert.

These considerations apply to a wide range of thermochemical energy storage systems and thermal transformer appliances designed to work with solid sorbents and water vapor under atmospheric pressure or even below, as shown on Fig. 1. The heat and mass transport properties have to be maximized for reactors shown on Fig. 1a and b. The optimization of the volume for the configuration from Fig. 1c implies the coexistence of reacted (hydrated) and unreacted (dehydrated) material fractions in a stratified storage tank. This case corresponds to a moving bed, for instance a fluidized bed. In this case, it is required that the water migration would be slow enough, so that the dehydrated material would not be contaminated by the hydrated material.

The proper design of the reactive bed (see Fig. 1a–c) by the means of computational fluid dynamics (CFD) usually requires the knowledge of parameters such as thermal conductivity, water diffusivity in the material and/or information on the bed permeability [3,4,22–29]. This issue is hard to tackle, since these values depend on several phenomena, the major of which are: real heat conduction inside the solid; free/forced convection around the shaped/powder-like material for thermal conductivity; heat and mass transport inside the single particle.

In the above-mentioned simulation works, thermal conductivity and

water diffusivity values were rarely obtained from direct measurements. The CFD methods used also a set of mathematical correlations for these parameters that must be first obtained using laboratory experimental methods.

Regarding thermal conductivity, devices that expose a sample to a local heating (plate or wire) and monitor thermal transients were used or developed, to get thermal conductivity and/or diffusivity ([30], “transient hot strip”: [31], “hot wire”: [32,33]). Such methods have already been tested in the case of salts for thermochemical storage [34] and phase change materials [35], with a moisture controlled atmosphere in the latter case. Benchmarks have been taken for composites of the same family in [32,36] and for pure silica. It has to be noted that it is appropriate to account for the thermal conductivity of the different phases, like in [22], where distinct values were taken for MgSO_4 and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. The same authors used a simple mixing rule between the solid and the gas [22]. In the work of Gaieni et al. [28], the Zehner-Schlunder relationship was used for the effective thermal conductivity [37], while Mette et al. [26] used the Winterberg relationships for thermal conductivity [38]. A review of correlations for the thermal conductivity of packed beds is given in [37].

Nevertheless, these works were related to a simple solid sorbent, being in contact with water vapor, and not to a composite material, for which the heat and mass transfer phenomena are more complex to tackle. Indeed, the heat and mass transfer rates are expected to depend on the way the salt crystals are being integrated to the supporting porous matrix, in addition to the above-mentioned phenomena. The PROMES group proposed and applied a framework based on a salt-in-matrix composite, when the matrix is much more heat conductive than the salt. By analogy with mass transfer, they introduced the concept of thermal tortuosity, to account for the more complex heat flow pathway. It was applied to MnCl_2 incorporated in a carbon matrix [3,16].

On the account of water diffusivity, it can be measured using water concentration profiles in a fixed packed-bed filled by the composite material and applying the Hall method. The latter is specifically suited for the concentration dependent diffusivity [39]. The obtained results can be used for water vapor migration modelling, based on the correlations like the Chen-Otmer equation mentioned in [27], but it does not apply directly to biphasic solids like in the present work. A review of existing correlations, that are applied typically to cylindrical packed bed, is available in [40], with a distinction between the transversal and longitudinal dispersion coefficients, and the influence of parameters like the particles diameter and the fluid velocity.

This work focusses on the macroscopic transport properties investigation of a novel composite material using CaCl_2 encapsulated into mesoporous silica gel. The pure salt is able to store 516 kW h m^{-3} of hexahydrate of CaCl_2 , considering the gain/loss of 5 mol of water per mole of CaCl_2 . It is non toxic and particularly cheap. An improved composite was proposed based on silica gel and 43 wt.% of CaCl_2 : a high energy storage density of 211 kW h m^{-3} (upgradable) was found

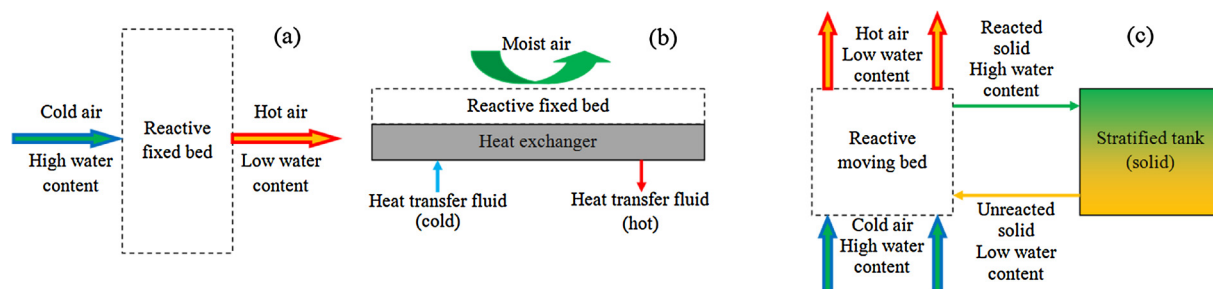


Fig. 1. Thermochemical processes and apparatus concerned by the present work. The process is shown during heat production: a) Fixed packed-bed reactor; b) Reactor (adsorber) with heat exchanging surface coated by the material (sorbent); c) Moving bed reactor with separate material (sorbent) storage.

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