



Performance characterization of salt-in-silica composite materials for seasonal energy storage design



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ABSTRACT

This work presents the results of the performance characterization for novel salt-in-silica composites, destined for seasonal energy storage. The materials were synthesized using the Davisil® silica gel to support the hygroscopic inorganic salts of calcium chloride (CaCl_2), magnesium chloride (MgCl_2) or strontium bromide (SrBr_2). The experiments were carried out on an open sorption laboratory setup under constant hydration conditions. The sample mass was 245 g, which is representative of a prototype control volume of 0.5 l, and the nominal air flow rate was 215 l min^{-1} . Energy storage densities between 70 and 145 kWh m^{-3} of control volume were experimentally found at $30 \text{ }^\circ\text{C}$ (inlet air temperature) and for different inlet air relative humidity levels. Average specific thermal powers in the range between 93 and 311 W kg^{-1} were measured. Based on the experimental results, the design and upscaling of the seasonal energy storage were demonstrated. The best feasible energy storage densities ranging from 50 to 90 kWh m^{-3} of up-scaled reactor were predicted to deliver 1000 W of rated thermal power.

1. Introduction

The solid/gas thermochemical sorption phenomenon appears to be a promising and effective technology in the area of thermal energy storage applications. Targeted applications are domestic hot water production, building space heating/cooling, and refrigeration processes using thermal solar energy or waste heat. Recent results in the fields of novel material synthesis [1–3], reactor and component design [4–6], and large-scale plant implementation [7–9] exhibit clear proof of the constant advancements towards technological fulfillment. The main challenges, that both ongoing and past research projects have tried to address, can be summarized as the development of compact and low-cost thermal energy storage concepts with high thermal power and energy density [10].

Concerning sorbents, the current studies are mainly focused on hygroscopic solids and selective water sorbents, as well as on chemical hydration reactions on metal hydroxides. These, for environmental reasons, are considered to offer the best compromise between energy density and the target operating conditions (charging and discharging temperatures and pressures), particularly for building space heating applications [11–18]. The highest energy densities, up to 630 kWh m^{-3} of bulk storage material, are achieved for inorganic hygroscopic salts

($\text{SrBr}_2/\text{H}_2\text{O}$ [19] as an example) for temperatures ranging from 30 to $80 \text{ }^\circ\text{C}$. However, the major drawbacks of pure hygroscopic salts, related to chemical and cyclical stability, hysteresis phenomenon and unsteady hygrothermal behavior, along with corrosion problem, extremely limit the development of energy storage prototypes.

In order to overcome these drawbacks, and to improve the thermodynamic properties of reactive solids, new composite materials based on silica gels (SGs), zeolites, metal-organic frameworks (MOFs) or silica-alumina with confined inorganic hygroscopic salts, the so-called *salt-in-matrix* (SIM), have been synthesized [20–24]. For these materials, the energy density can reach up to 200 kWh m^{-3} of storage material for hydration and dehydration temperatures between $30 \text{ }^\circ\text{C}$ and $80 \text{ }^\circ\text{C}$ respectively, and a water vapor pressure of 12.5 mbar.

Despite the significant progress made in material synthesis, the apparent energy densities of the constructed prototypes using these materials are lower than the so-called intrinsic energy density of the storage materials themselves. The results of IEA-SHC Task 32 demonstrated experimentally that the drop in energy density can vary from 25% to 68% depending on the prototype characteristics and testing protocol for various materials [25].

The early experimentations on the SOLUX [26] modular reactor prototype working with $\text{SrBr}_2/\text{H}_2\text{O}$ (using 9.1 wt.% of inert expanded

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Nomenclature*Common abbreviations*

COP	Coefficient of performance
MOF	Metal-organic framework
R.H.	Air relative humidity
SG	Silica gel of Davisil®
SIM	Salt-in-matrix

Symbols

A_b	Surface area of sorption cell [m^2]
C_p	Specific heat capacity [$J kg^{-1} K^{-1}$]
k	Average sorption rate [$kg s^{-1}$]
\dot{m}	Mass flow rate [$kg s^{-1}$]
m_s	Bulk mass of material [kg]
p	Gas pressure [$mbar$]
\dot{Q}	Specific thermal power [$W kg^{-1}$]
T	Temperature [$^{\circ}C$]
t	Time [s]
x	Water uptake [$kg_{H_2O} kg_{solid}^{-1}$]
y	Degree of hydration advancement [%]
V_c	Prototype control volume [m^3]
V_b	Volume of packed bed of particles [m^3]
w	Air humidity ratio [$kg kg^{-1}$]

Greek symbols

ΔE	Energy storage density [$kWh m^{-3}$]
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ΔH	Enthalpy change [$J kg^{-1}$]
Δx	Water uptake loading lift [$kg_{H_2O} kg_{solid}^{-1}$]
ε	Effectiveness
λ	Thermal conductivity [$W m^{-1}K^{-1}$]
ρ	Density [$kg m^{-3}$]

Subscripts

0	Initial state
∞	Terminal state
65	Threshold limit of 65% of the degree of hydration advancement
A	Relative to air, carrier gas
av	Average value
b	Granular bed
e	Equilibrium state
ev	Relative to vaporization process
hx	Relative to heat exchanger
in	Reference to input of system
j	Relative to a certain threshold level
L	Relative to axial dispersion
out	Reference to output of system
R	Relative to reactor
s	Solid material
u	Relative to user conditions
w	Relative to water
v	Relative to water vapor

graphite as binder) showed a drop of 61% when comparing the apparent energy density of the reactor ($60 kWh m^{-3}$) and the energy density of the storage material ($154 kWh m^{-3}$ of reactive composite material layer). A high apparent reactor energy density of $203 kWh m^{-3}$ has been obtained for the ESSI modular apparatus [19], which is a drop of 48% of the energy density of the reactive material ($388 kWh m^{-3}$ for a 75 mm bed thickness of $SrBr_2/H_2O$). The experiments with zeolite 13XBF from the COMTES prototype [27] (vacuum tight module with immersed heat exchanger) showed an energy density of $77 kWh m^{-3}$ corresponding to 64% of the reachable energy storage density of the material. Zondag et al., [28] presented the results of studies on the hydration process of $MgCl_2/H_2O$ within a laboratory open sorption prototype for thermochemical energy storage purposes. The authors pointed out the obvious shortcomings of the apparent energy density drop (experimental value is $139 kWh m^{-3}$ vs. theoretically predicted $278 kWh m^{-3}$ of porous bed). The characterization of the composite material zeolite 13X + $MgSO_4$ was carried out in a laboratory scale macro-reactor by Hongois et al. [29]. The experimental value of the energy density corresponded to 45% of the theoretical value. The authors indicated that the energy density is highly sensitive to air humidity.

The drop in the apparent energy density is directly due to the limitations of the heat and mass transfer phenomena within the system, the upscaling and the operating conditions. The design of closed storage systems usually requires a large heat exchanging/solid supporting area. The prototype modules often integrate a heat exchanger coated with granulated material [30], while other configurations host a specially designed uncoated heat exchanger [9]. In both cases the contact resistance between material's particles, the corrosion of the heat exchanger surface and thus the effective thermal conductivity are critical for the delivery of useful thermal power to the end-user. For these configurations, the design efforts are directed for the improvement of effective thermal conductivity (surface coating techniques [31,32],

corrosion mitigation techniques [33], and utilization of high thermal conductivity additives [34]).

Open prototype concepts are usually designed to be operated under atmospheric conditions with moist air as a heat/mass transfer fluid and no special heat exchanger is needed [4]. The typical configurations exploit the forced fluid circulation over a large specific surface area of the granular or shaped material [5,6]. However, major problems are the increased pressure drop through the material layer and non-homogeneous sorption due to preferential fluid flow. Another way to enhance the energy density of storage systems, with, however, a significant affection of the permeability properties, is material shaping using consolidation and extrusion techniques [35,36] or the use of binders and foams [37]. Fluidized-bed reactors have gained in interest in thermochemical energy storage applications due to the heat and mass transfer enhancement that they allow, but the apparent reactor energy density is rather poor due to the loss of density of the fluidized medium compared to packed bed configurations [18].

Therefore, the apparent energy density of any prototype is certainly being decreased, not only on the material level (through the use of binders for material shaping or high thermal conductivity additives), but also, and mostly, at the component size/system level (due to the integration and coating of heat exchangers or by other auxiliary devices to control the fluid streamlines).

The present work is devoted to the study of working performances under constant hydration conditions of several recently synthesized SIM composite materials (silica gel + hygroscopic inorganic salt) using laboratory apparatus. The objective consists in the experimental measurement and prediction of performance characteristics (e.g. energy storage density, thermal power, COP) of the studied materials in open sorption reactor for the scope of selected operating conditions and sizing parameters.

The proposed materials resolve the multi-cycle and morphological stability problem, in comparison with pure salts, as discussed in

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