Applied Energy 190 (2017) 1184–1194

Contents lists available at ScienceDirect

Applied Energy

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

A new composite sorbent based on $SrBr_2$ and silica gel for solar energy storage application with high energy storage density and stability

Emilie Courbon [a,*], Pierre D'Ans [b], Anastasia Permyakova [c], Oleksandr Skrylnyk [a], Nathalie Steunou [c], Marc Degrez [b], Marc Frère [a]

[a] Department of Thermodynamics and Mathematical Physics, Université de Mons, Boulevard Dolez 31, B-7000 Mons, Belgium
[b] 4MAT Department, Université libre de Bruxelles (ULB), Avenue F.D. Roosevelt, 50 - CP 194/3, B-1050 Bruxelles, Belgium
[c] Institut Lavoisier, Université Versailles-Saint-Quentin-en-Yvelines, Université Paris Saclay, 45 Avenue des Etats-Unis, 78035 Versailles Cedex, France

HIGHLIGHTS

- Synthesis of a new composite material based on $SrBr_2$ and silica gel.
- High energy storage density of 203 kW h/m^3 is reported for thermal energy storage applications.
- High cycling stability is reported.

ARTICLE INFO

Article history:
Received 10 October 2016
Received in revised form 21 December 2016
Accepted 15 January 2017
Available online 21 January 2017

Keywords:
Composite
Silica gel
Strontium bromide
Sorption isotherms
Energy storage

ABSTRACT

The excellent matching between the sorption and desorption temperatures of hexahydrated $SrBr_2$ and those required for solar heat storage for building applications, the high heat of reaction (67.5 kJ/mol of water) coupled with the gain/loss of 5 mol of water per mole of salt make this salt an appealing sorbent for solar thermal energy storage applications coupled to space heating. Due to the morphological instability of this salt, it is necessary to incorporate it in a porous matrix as a composite sorbent. A new composite material for thermochemical energy storage applications was developed. It consists of a mesoporous silica gel impregnated by strontium bromide with salt content equal to 58 wt.%. The structure and the sorption properties of the composite were characterized by SEM-EDX, temperature dependent XRD, XRF, and N_2 sorption measurements. The salt is homogeneously distributed inside the pores of the silica gel. Water sorption isotherms were measured between 20 °C and 80 °C, which enabled us to understand the sorption mechanism. A mathematical model was developed and used to fit the experimental data in order to predict the sorption behavior of the composite at different conditions (influence of temperature and pressure conditions on the cycle loading lift and energy storage density). The interest of using such a composite for thermal energy storage application is then discussed (thermal energy produced by solar collector and used for space heating). A high cycle loading lift of 0.22 g/g is obtained corresponding to an energy storage capacity of 230 W h/kg and an energy storage density of 203 kW h/m^3 of packed bed composite (between 30 °C and 80 °C at 12.5 mbar) is reported, with an excellent stability over 14 sorption/desorption cycles. The sorption kinetics of this composite is enhanced compared to pure salt. Test on a laboratory scale open type reactor gives a maximum specific thermal power of 200 W/kg and a mean specific thermal power of 92 W/kg at 30 °C and 12.5 mbar for an extent of reaction of 0.68.

1. Introduction

Nowadays it is increasingly important to improve the share of renewable energies in final energy consumption in order to reach the objectives defined by the European Commission (20% of final energy produced from renewables in 2020, and 27% in 2030). Solar energy is one of the most interesting solutions among renewable energy resources as it can be converted easily into heat or electricity. The main problem when using such an energy source is its unfair time distribution, which may cause a mismatch between needs and availability. Seasonal storage of solar energy is required to collect energy during summertime to be used in winter. The need for seasonal solar thermal energy storage systems is crucial

* Corresponding author.
E-mail address: Emilie.courbon@umons.ac.be (E. Courbon).

http://dx.doi.org/10.1016/j.apenergy.2017.01.041
0306-2619/

for space heating application in temperate and cold climate countries. The relevance of such a technology is even more stringent in EU28 which adopted a regulation called Nearly Zero Energy Building Directive to be effective in 2020 for new buildings [1]. The low energy consumption of these new buildings (e.g. 3000 kW h/year for space heating of a 100 m^2 dwelling in Belgium) will have to be mainly covered by local renewable energy sources. In countries with high heat demand buildings, the optimal solution is to use a heat pump while the electricity consumption is totally covered by PV production. To avoid massive electricity production/consumption during summer/winter, a more elegant solution would be to avoid the electrification of the heat demand by using thermal solar collectors and seasonal heat storage [2]. Seasonal heat storage for space heating is not considered as a completely mature technology. It requires to store huge energy quantities during several months with reduced losses to be recovered later on at a temperature level which fits the application. Up to now, demonstration cases [3] were developed relying on sensible heat technologies (water tanks, gravel pits, aquifer and underground energy storage); the heat storage system is centralized at the level of a district thus requiring a district heating grid. One of the most well-known case is the Drake Landing Solar Community which reaches a 100% solar coverage of the heating needs of a 52-dwelling district in 2015–2016 [4]. It uses a 30,000 m^3 underground heat storage with an energy density of approximately 25 kW h/m^3. In order to reduce costs and size of seasonal heat storage systems, higher energy densities are required, which is not possible when considering sensible heat storage technologies. Thermochemical storage technologies (sorption systems) present high theoretical energy storage densities (up to several hundreds of kW h/m^3) and low losses (energy is stored through chemical bonds rather than through temperature lift). This is in accordance with long term energy storage requirements, particularly when a chemical sorbent is used [5–8]. In sorption systems, during summer, the energy is stored thanks to the desorption process, which needs heat provided by the solar collectors, whereas during winter, the heat is produced by the adsorption process, which is exothermic.

While thermochemical storage is a promising technology for ensuring a 100% solar coverage of the heat demand in buildings through seasonal operation, its Technology Readiness Level (TRL) remains low (4–6). Further developments are needed in terms of storage material, reactor and system for first demonstration cases to be developed [9,10]. In terms of storage material, high energy storage density (kW h/m^3) or/and storage capacity (W h/kg) are the key parameters to consider, as well as non-toxicity, availability and cost [11,12]. An energy storage density at equilibrium of 150 kW h/m^3 may be considered as a minimum target value to ensure a real breakthrough compared to sensible heat storage. High cycling stability is another crucial parameter for long life operation of the system (at least 25 cycles). Reactor design must be performed in such a way that the maximum heat flow to be stored during summertime and provided during wintertime for ensuring internal thermal comfort may be effectively stored/produced. Thermochemical systems generally exhibit high kinetics at the starting point of the reaction and a poor one when approaching equilibrium. One of the main challenges when designing the reactor is to bring the system close to equilibrium for ensuring a high energy storage density while keeping the reactor size acceptable. In terms of system, the main challenge is to size all the components (solar collector surface area, heat emission system within the building) so that the reactor/whole system may operate in favorable conditions (conditions that foster the global system performance: e.g. low heat emission temperature, optimized desorption temperature for maximizing both the energy storage density and the solar collector efficiency). These challenges must be performed in an integrated way [13]. For example, the energy storage density at equilibrium of a given storage material depends on the conditions of use of the system (e. g. temperatures at which the heat must be stored/recovered). Those conditions mainly depend on the different components of the complete storage system (type of solar collector, heat distribution system within the house, closed or open reactor). Assuming too optimistic conditions could lead to consider a material as promising without any guarantee of success once tested at the prototype level.

This research work mainly focuses on the development of a new storage material for thermochemical storage (solar heat for space heating application) while taking into account all the required specifications for a final use in a heat storage prototype (e.g.: high energy storage density in working conditions close to the application, high cycling stability and appropriate kinetics).

Concerning the storage material, chemical sorbents that were identified for solar thermal energy storage/space heating applications are inorganic hydrated salts which present some disadvantages when used as pure materials. For example, the hydration/dehydration process may produce the swelling of the salt, due to a change of crystal structure, which may limit the heat and mass transfers [14]. A hard crust is also observed for some inorganic salts due to the agglomeration of partially hydrated salt. This problem was observed for example for $MgCl_2$, $MgSO_4$ [15], $CaCl_2$ [16] and $SrBr_2$ [17]. Problems of aggregation or pulverization are also observed when a salt is used in a thermochemical storage reactor [18]. Concerning chlorides, they tend to form a gel-like substance due to the melting of the hydrated salt [19]. In order to limit those problems, the salt may be confined into the pores of a porous matrix and hence used as a composite sorbent [20, 21]. Composite sorbents are expected to exhibit in-between sorption properties compared to the physical adsorbent used as the porous matrix and the inorganic salt. As a consequence, one could control the sorption capacity by varying the porous matrix structure, the chemical structure of the hydrated salt and/or the amount of salt inside the pores.

When stabilizing a salt by the synthesis of a composite, a compromise must be found between the incorporation of a high salt content into the pores of the matrix to keep a high energy storage density, and a good stability of the composite material under successive hydration/dehydration cycles. The synthesis procedure must be optimized for such an objective and rely on a comprehensive set of structural data that allow us to evaluate the long term stability of the composite. Structural data may also be used, together with energy performance measurements in a wide range of conditions, to propose the sorption mechanism and hence, a reliable model for sorption properties calculation to be used as a tool for engineers.

In the present study, a new composite based on $SrBr_2$ and silica gel was synthesized in order to stabilize the salt and to facilitate its future use in seasonal storage system for space heating application. The choice of the salt and the matrix was based on a literature review which will be detailed in the following section. In order to increase the composite cycling stability, a new and original synthesis protocol was developed, which allowed us to reach a high salt content, homogeneously distributed into the pores of the matrix. The composite structural and sorption properties were determined. The efficiency of this material for solar storage applications was evaluated on small samples (a few tenth of mg) by measuring the cycle loading lift, the energy storage density and the cycling stability, in conditions close to the real ones in terms of temperature and pressure. The adsorption temperature was set to 30 °C, while the desorption temperature was set to 80 °C, easily reachable with thermal solar collectors. For both adsorption and desorption steps, the water vapor pressure was set to 12.5 mbar, corresponding to the saturation vapor pressure at 10 °C, representative of condensation or evaporation conditions