# State of the art on gas-solid thermochemical energy storage systems and reactors for building applications

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Abstract

Thermal energy storage (TES) is moving towards thermochemical materials (TCM) which present attractive advantages compared to sensible and phase change materials. Nevertheless, TCM are more complex to characterize at lab scale and also the implied technology, which belongs to the chemical engineering field, needs to be contextualized in the TES field. System configurations for thermochemical energy storage are being divided into open/closed storage system and separate/integrated reactor system. Reactors, which are the core of the system, are the focus of this paper. Different gas-solid thermochemical and sorption reactors for building applications are reviewed from lab to pilot plant scale, from 0.015 to 7850 $dm^3$. Fixed bed reactors are the most used ones. Mainly, mass transfer is limiting to achieve the expected energy density. The geometry of the reactor and contact flow pattern between phases are key parameters for a better performance.

*Keywords:* Thermal Energy Storage (TES); Thermochemical Material (TCM); Reactor; Energy density; Heat and Mass transfer; Sorption.

## 1. Introduction

There is a global aim to reduce energy consumption since humans are using finite resources and contributing to environmental pollution. A part of becoming aware of this problem, engineers and scientists are focused on renewable energy sources and on improving energy efficiency of heating and cooling systems. Thermal energy storage (TES) is needed to capture thermal energy when available and to release it when demanded and for temperature control. Thermal storage applications have been proved to be efficient and financially viable, yet they have not been exploited sufficiently [1].

Regarding TES systems for building comfort applications, several big projects are being carried out, for instance Dronninglund Solar District Heating Plant in Denmark is now established. It consists of 37,000 m² collectors (26 MWth) and 60,000 $m^3$ seasonal storage. In February 2014, the Dronninglund Solar District Heating Plant started operation serving the 1,400 connected customers. The collector field together with the seasonal storage covers around 50% of the total annual heat load [2]. Present heat production in kW and W/m$^2$ is available in [3].

TES systems can be classified by the process undergone by the storage material: sensible, latent and thermochemical. Sensible storage is based on transferring heat to the material which leads to an increase of the material temperature itself. Latent storage implies storing heat when a phase change of the material (PCM) occurs. This last process usually carries also sensible heat storage, before and after the phase change process. Then, thermochemical storage is based on thermochemical materials (TCM) undergoing either a physical reversible process involving two substances or reversible chemical reactions (Eq.1). Endothermic processes absorb energy (heat), which can be stored as long as desired until the reverse (exothermic) process is forced. When the exothermic process takes place, the released heat can be then used for instance, for domestic hot water (DHW) and heating building applications. Since the storage is based on the molecular bonds formation, the energy is neither lost to the ambient nor transformed if the material is kept at certain conditions. This great advantage makes the TCM suitable for long-term storage, also known as seasonal storage, since heat from summer can be stored to provide heat at winter times.

$$A + Heat \leftrightarrow B + C \quad \text{Eq. 1}$$

TCM materials have other advantages when compared to sensible and phase change materials (PCM). TCM present higher energy densities [4], which lead to a lower volume of the storage tank, thus compact systems. On the other hand, corrosion of metals used to build up reactors containing TCM is one of the main drawbacks to overcome. From a material point of view mass transfer is a key issue when selecting the material. Salt hydrates (which are one big group of TCM) tend to form a compact block which is inhibiting the reversibility of the reaction. Furthermore, additional heat is needed to reach the discharging reaction temperature.

Depending on the system configuration that is chosen to implement TCM for building applications (see section 2), the equipment is composed of the reactor, heat exchangers, vessels, evaporator/condenser, solar collectors, valves and piping. In order to design the main equipment, the reactor, several steps need to be followed. From the system design further research is still needed to resolve practical aspects before commercial implementation [5]. And focusing on the reactor, there is still a big field of research to promote mass and heat transfer playing with the inside geometry and/or reactor kind. The design and operation of reactors nowadays require computer skills, but such computation must be based on a firm grasp of the principles of chemical reaction engineering. First, reaction kinetics, thus reaction rate, is needed to be experimentally determined for the specific operating conditions [6]. Then, once the equation of reaction rate is experimentally obtained, mass and heat balances are formulated depending on the reactor type. All these equations gathered give variables profiles (concentration, pressure, temperatures, etc.), volume, and let do predictions for further cases as well as optimization.

The main objective of this paper is to review the available equipment currently used for thermochemical energy storage, concerning all system configuration and especially gas-solid reactors for building comfort applications, providing obtained results, at lab and pilot plant scale. Furthermore, gas-solid chemical reactors already available in the literature and industry are exposed to be related with the developed ones for TES by TCM.

## 2. Gas -Solid TCM reactors and system

Different concepts and applications based on TCM have arisen to fulfil the global aim to reduce energy consumption and to efficiently use renewable energies or to use waste heat. Prototypes for both high temperature and building applications are being built up to test this concept. For instance, directly irradiated rotary kiln for high temperature reactions (around 900 ºC) has been set up and performed for thirty cycles with no evident degradation of the material [7].

More effort is needed in the system design part regarding TCM reactors for building comfort. This application implies that a solar collector should be able to provide the charging reaction temperature (maximum 150 ºC) to the reactor containing the TCM. Also, a big challenge is that the volume of the final system should fit in a single family house and be cost competitive to the actual heating systems.

As shown in Section 4.1, reactors can be classified by the present phases of the reactant materials. Here, the aim is to focus on gas-solid TCM (Eq.2) and building comfort applications (i.e. heating, cooling, and domestic hot water (DHW)), and being water the gas reactant (working fluid).

$$H_{(s)} + Heat \longleftrightarrow D_{(s)} + H_2O_{(v)} \quad \text{Eq. 2}$$

In TCM TES field, the chemical reaction is used for the production of energy instead of a specific product. The operating principle is to charge (dehydrate) the solid TCM with solar heat from a solar collector. This endothermic reaction releases water vapour. The storage process is therefore based on maintaining separately released water from the dehydrated TCM. When combining again the dehydrated TCM and water vapour, heat is released and can be used for space heating and DHW.

Despite the reactor is the core of the system, other essential concepts and components are needed to be considered for TES: the working fluid, a low heat source and an evaporator/condenser (depending on the system).

The working fluid is usually water because of its high vaporization enthalpy, availability, non-toxicity and low price. Ammonia is also a candidate [8], but then another heat exchanger (ammonia/water or ammonia/air) is needed to provide the heating fluid to the building.

**2.1 TCM systems classification**

The existing thermochemical energy storage system configurations can be divided following an overall vision of the complete system.

2.1.1 Separate or external vs. integrated reactor

In the integrated reactor system, the absorption/release of energy (reaction) occurs within the storage vessel while the separate reactors concept consists in transporting the TCM from the storage vessel to the reactor and to another storage vessel, after reacting, as illustrated in Figure 1.

The integrated concept requires no solid material transport, thus less pump power consumption (see Figure 2, left). Nevertheless, all the material, instead of a portion, needs to be preheated to reach the discharging temperature and the control of the reaction is more complex. In the separate reactor concept the material is transported between the reactor and the material storage vessel, therefore more vessels are needed (at least two more). The advantage of being in separate vessels is that the reaction is reduced to only a small part of the total material amount [9], so the reactor volume is much smaller which leads to a lower pressure drop and less complex process control.

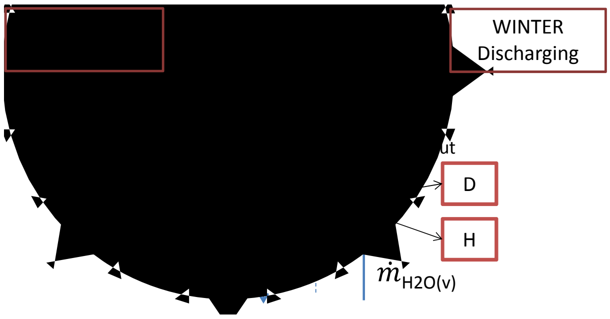


Figure 1. External reactor with an open configuration. Where H: hydrate and D: dehydrate (Eq.2)

Another possible classification would look at the type of reactor (see section 4.2): fixed bed reactor, moving bed, and fluidized bed. Specifically, in TCM, fixed bed is the most used one.

Generally, fixed bed reactors are considered to be the most appropriate reactor configuration for hydration/dehydration reactions [10]. Since in fixed bed reactors heat and mass transfer are critical, Zondag et al. [11] suggest either to stir, to increase the active surface area in it, and/or to purge inert gases of the reactor. In moving bed reactors, there may be problems with the heat transfer within the reactor, but metal fins are suggested to enhance it [12].

### 2.1.2 Open/closed storage systems

The main difference between closed and open systems is the storage of the gas reactant (working fluid). Looking at Figure 2, right, in closed configurations, water circulates in a hermetically closed loop. In order not to store released water in vapour state (because of the high volume it would require), it is condensed until it is needed again. At that moment, the evaporator will return water in vapour state. Also, a water reservoir is needed. In open configurations, water is taken and released to the ambient air.

A low heat source is needed to deliver energy required for water evaporation ($Q_{evap}$ Figure 2, right), for closed systems. This energy has to be either extremely low cost or free, and additionally has to come from a heat source of at least ~5°C. Ground boreholes and solar collectors are the most used candidates to act as low heat source. Closed systems allow adjusting the operating pressure of the working fluid. In open systems, the working fluid should be a substance that can be released to the atmosphere, usually water [13]. Pressure is not a variable since these systems are working opened to the atmosphere and pressure is set to the atmospheric pressure. Moreover, weather conditions are limiting and an analysis should be carried out to define whether the ambient moisture is sufficient for a good discharging rate. Otherwise, an additional humidifier is required to make the air wet to react with the TCM.

Closed systems are able to reach higher output temperatures for heating applications compared to open systems. Furthermore, they can supply lower temperatures for cooling [13].

The geometrical parameters and the dynamical behaviour of the closed sorption systems are strongly related. The available temperature depends on the pressure of the sorbate and the driving force is limited by the external temperature ranges - the low temperature energy source - the mid temperature source/sink and the high temperature energy source, which is aimed to be a solar collector [14].


Figure 2. Open (left) vs. closed (right) systems with integrated reactor.

Michel et al. [15] compare closed and open modes with the same TCM ($SrBr_2 \cdot 1H_2O$/ $SrBr_2 \cdot 6H_2O$) and simulation results show similar global performances, 0.96 and 1.13 W/kg, respectively.

## 3. TCM materials/reactions

### 3.1 Classification

In the literature different attempts have been made to classify the studied storage materials, also known as thermochemical materials (TCM). Absorption, adsorption and chemical reactions are the thermochemical processes accepted.

Absorption and adsorption can either be physical or chemical. As explained by Srivastava and Eames [16], adsorption is a surface phenomenon taking place at the interface of two phases, in which cohesive forces including hydrogen bonding and van der Waals forces act between the molecules of all substances. In this case, there is no change in the molecular configuration of the compound.

On the other hand, in essence, absorption involves substances in one state being incorporated into the bulk volume of another substance in a different state, whereas adsorption involves substances being adhered to the surface of another substance. Sorption is a general term used to refer to both.

Then, there are also the chemical reactions where molecular configurations change. Chemical energy consists of using a source of energy to excite a reversible chemical reaction, being exothermic in the discharge and endothermic in the charge.

When looking at the literature information regarding the TCM classification is confusing and sometimes differs. Although the classification of the TCM is out of the scope of this paper a compilation of the studies published so far is presented next. From this information it is concluded that further studies should be performed in order to establish a clear classification of the TCM reactions.

N'Tsoukpoe et al. [18] consider that sorption comprises physical and chemical, absorption and adsorption. Also, chemical solid/gas reactions are considered as chemisorption (chemical adsorption) as shown in Figure 3, where salt hydrates would belong to.

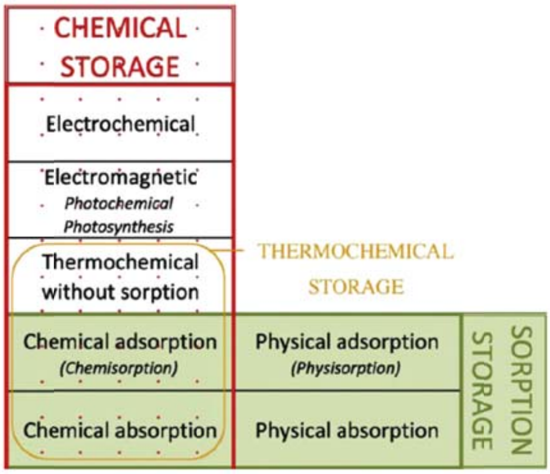


Figure 3. Chemical and sorption storage classification [17]

In [180] Abedin and Rosen suggest to refer to the entire category as chemical energy storage and to divide it into sorption and thermochemical reactions, where sorption includes adsorption and absorption. Here, salt hydrates would be in the thermochemical reactions group.

In [19] Tatsidjodoung et al. thermochemical heat storage materials comprises two big groups: sorption phenomena materials, in within adsorption and absorption are found, and chemical reaction materials, which is also divided into pure and composites thermochemical materials. Here, salt hydrates belong to chemical reactions, pure thermochemical materials.

Xu et al. [20] purpose classification for chemical storage is to divide the materials into three big groups: adsorption, absorption, and chemical reaction. Salt hydrates are considered in the adsorption group.

Salt hydrates are one of the most promising materials for TCM applications. Salt hydrates tend to form compact blocks hindering the diffusion of water vapour through the material, which results in less energy involved. Thus, a possible solution is to use host matrices as a support for the TCM vapour transport, thus enhancing mass transfer. These materials, usually called matrix or host, can be either an inert (cellulose, expanded natural graphite, metal foam) or an adsorber (zeolite, activated carbon, silica gel) and thus contributes to the energy involved in the reaction, being exothermic the adsorption process. Nevertheless, Michel et al. [21] demonstrated experimentally that adding a porous binder, vermiculite, to $SrBr_2/H_2O$ reaction does not lead to any enhancement of the thermal power due to the decrease of reaction time and salt bed permeability (see Table). When adding a matrix, material properties, such as sorption equilibrium, energy density, porosity, etc. and compatibility of both TCM and matrix and container material shall be determined again in the specific operating conditions.

In this review TCM concerns all chemical reversible processes (also composites) specifically, gas-solid ones for building applications and moreover, physisorption is considered. Chemical and physical absorption are out of the scope.

3.2 TCM candidates for building applications

Thermochemical material research encompasses several fields. One big field is materials research, which is focussing on material selection, enhancement and characterization. Regarding TCM building applications, main requirements are [22]:

- high energy density
- non-toxic
- non-flammable
- low cost
- reachable temperature reaction by a solar collector
- non-corrosive
- stable after several hydration/dehydration reactions

Some of the most attractive TCM under study for building applications are listed in Table 3 and in [23]. What makes them viable for building applications is that the reaction temperature is below 150 ºC (known as the maximum reachable temperature by a solar collector). When designing the system and selecting the TCM, there are important points to take into account: (1) Vacuum vs. atmospheric operation conditions since this is influencing reaction temperatures and is closely governed whether the system is designed to work in open or closed configuration (see Section 2.1.2). (2) Energy density, which is influenced by the sample scale (lab or reactor), the geometry of the reactor, the used technique to characterize it and also on the operating conditions such as evaporator and reactor temperatures (when working in close systems configurations). There is no standard procedure to determine their thermophysical properties, yet.

Table 1. Theoretical and experimental energy density, reaction temperature and water vapour pressure of TCM

| Reaction (TCM) (solid ↔ solid + gas) | Theoretical energy density ($GJ/m^3$) | Experimental energy density ($GJ/m^3$) | Reaction Temperature (charging/ discharging) (ºC) | $p_{(H2O)}$ (mbar) | Reference |
|---|---|---|---|---|---|
| $MgCl_2·6H_2O$ ↔ $MgCl_2·H_2O + 5H_2O$ | 2.5 | 0.71 | 150/30-50 | 13 | [22] |
| $MgCl_2·4H_2O$ ↔ $MgCl_2·2H_2O + 2H_2O$ | 1.27 | 1.10 | 118/n.a. | 13 | [24] |
| $CaCl_2·2H_2O$ ↔ $CaCl_2 + 2H_2O$ | 1.1 | n.a. | 95 | n.a. | [22] |
| $CaCl_2·2H_2O$ ↔ $CaCl_2·H_2O + H_2O$ | 0.60<br>0.72 | n.a. | n.a./174<br>95/35 | n.a. | [25,19] |
| $Al_2(SO_4)_3·6H_2O$ ↔ $Al_2(SO_4)_3 + 6H_2O$ | 1.9 | n.a. | 150 | n.a. | [22] |
| $MgSO_4·6H_2O$ ↔ $MgSO_4·H_2O + 5H_2O$ | 2.37 | 1.83 | 72/n.a. | 13 | [24] |
| $MgSO_4·7H_2O$ ↔ $MgSO_4·H_2O + 6H_2O$ | 2.3 | n.a. | 150/105 | n.a. | [25] |
| $MgSO_4·7H_2O$ ↔ $MgSO_4 + 7H_2O$ | 1.5 | n.a. | 122-150/122 | n.a. | [19] |
| $CaSO_4·2H_2O$ ↔ $CaSO_4 + 2H_2O$ | 1.4 | n.a. | n.a./89 | n.a. | [25,18] |
| $Na_2S·5H_2O$↔ $Na_2S·1/2H_2O + 9/2H_2O$ | 2.7 | n.a. | 80/65 | 13 | [26] |
| Zeolites 4A | n.a. | 0.58 | 130/65 | n.a. | [19] |
| $SrBr_2·6H_2O$ ↔ $SrBr_2·H_2O + 5H_2O$ | 2.3 | 2.08 | n.a. /23.5 | 20 | [21] |
| $SrBr_2·6H_2O$↔$SrBr_2·H_2O + 5H_2O$ and vermiculite | n.a. | 1.83 | n.a. /22.3 | 10 | [21] |
| $Li_2SO_4·H_2O/Li_2SO_4 + H_2O$ | 0.92 | 0.80 | 103/n.a. | 13 | [27] |
| $CuSO_4·5H_2O$↔$CuSO_4·H_2O + 4H_2O$ | 2.07 | 1.85 | 92/n.a. | 13 | [27] |

### 3.2 Characterization

For the further design of the TCM reactor and the corresponding system, several properties of these materials need to be known. An accurate characterization of the material is essential to develop and model the suitable reactor that will contain the TCM.

Researchers working on TCM characterization and selection are mainly using two coupled thermal analysis techniques: thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) as listed in Table 2. These techniques are also used in other fields and in the same field, TES, for sensible and PCM characterization [28]. With these techniques dehydration steps, energy released, associated temperatures, specific heat, phase diagrams and in some cases stability, can be evaluated. Furthermore, X-ray crystallography (XRD) provides information about the crystalline structure of the material, thus the hydrate state of the TCM. By means of scanning electron microscopy (SEM), the surface of the TCM grains before and after hydration can be observed and this information is useful to see how kinetics is governed by, and if there is degradation. A published study [29] shows how thermodynamic and kinetic properties of TCM are directly related to the structural and textural modifications when hydration/dehydration takes place.

Some of the analysed TCM by TGA-DSC techniques are shown in Table 2 with the applied methodology and obtained results. In [23] results from hydration experiments show big differences in heat released as a function of the sample thickness (since it influences in gas diffusion). Also, hydration has been performed at 25 ºC, but when performing at 50 ºC magnesium sulphate was unable to uptake water. Therefore, in the same study the authors present a self-developed setup, a reactor and evaporator, to characterize the TCM (see Section 4.2). Also, in [30] they present how the conversion is influenced by applying different heating rates of the TGA-DSC. Composites based of mainly an adsorbent and a salt hydrate or a mixture of salts is also being characterized by TGA-DSC technique. For instance, in [31] characterization of four different zeolites impregnated with magnesium sulphate are performed. Zeolites Na–Y and H–Y composites containing 15wt% $MgSO_4$ achieved the highest heats of hydration, 1090 and 867J/g respectively. Then, a complete study looking for the characterization of a composite based on attapulgite impregnated with different weight percentages of two TCM is presented in [32]. Usually, all these studies also present results with the abovementioned techniques.

Thermophysical properties such as energy storage, hydration/dehydration temperatures, density, specific heat, thermal conductivity, chemical and physical stability over hydration/dehydration cycles, kinetic data and phase diagrams are needed first for a material selection and all of them, except density and thermal conductivity, can be determined by combining TGA-DSC and XRD techniques,. From the literature it has been seen that these techniques offer some limitations when working with TCM and that other processes as mass transfer are influencing results. Therefore, when a complete information is required such as the influence of operating conditions on kinetic rate or on energy storage, other parameters as permeability, particles size, the effect of adding a gas diffuser, etc. and another setup such as a laboratory reactor (in the order of few kilograms), is necessary.

Table 2. TCM thermal analysis technique, applied methodology and obtained results of some characterized TCM

| TCM analysed | Technique | Methodology (heating rate, sample mass, pressure, ∆ T) | | Results | | Reference |
|---|---|---|---|---|---|---|
| | | Hydration | Dehydration | Hydration | Dehydration | |
| $MgSO_4 \cdot 7H_2O$ / $MgSO_4$ | TGA-DSC | Ms:5-50 mg<br>$p_{H2O}$= 2.3 kPa<br>T=25 ºC | Ms:10-50 mg<br>Trange:25-300 ºC<br>Heating rate: 1 ºC/min | 1.8 $GJ/m^3$ | 2.2 $GJ/m^3$ | [22] |
| $Ca(OH)_2/CaO$ | TGA-DSC | Ms:10 mg<br>T=30 ºC<br>$p_{H2O}$=19 hPa | Ms:10 mg<br>Heating rate: 5 ºC/min<br>$N_2$ atmosphere | 1823 J/g | 1209 J/g | [30] |
| $CaCl_2 \cdot 6H_2O/CaCl_2$ | TGA-DSC | Ms:10 mg<br>T=30 ºC<br>$p_{H2O}$=19 hPa | Ms:10 mg<br>Heating rate: 4 ºC/min<br>N2 atmosphere | 2629 J/g | 1153 J/g | [30] |
| $MgCl_2 \cdot 6H_2O/MgCl_2 \cdot 2H_2O$ | TGA-DSC | Ms:10 mg<br>T=30 ºC<br>$p_{H2O}$=19 hPa | Ms:10 mg<br>Heating rate: 5 ºC/min | 1551 J/g | 1344 J/g | [30] |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | N2 atmosphere | | | |
| Zeolites Na-Y + 15 wt% $MgSO_4$ | TGA-DSC | T=20 ºC $p_{H2O}$=1.3 kPa | Trange:20-150 ºC Heating rate: 2 ºC/min Helium atmosphere | 1090 J/g | n.a. | [31] |
| Attapulgite impregnated 20 wt% MgSO4/80 wt% MgCl2 | Calorimeter | Ms: 0.75 g T= 30 ºC 85% RH | - | 1590 J/g | - | [32] |
| $Li_2SO_4 \cdot H_2O/Li_2SO_4$ | TGA-DSC | Ms:10 mg T= 25 ºC $p_{H2O}$=13 mbar | Ms:10 mg Trange: 25-150 ºC Heating rate: 1 ºC/min | 0.77 $GJ/m^3$ | 0.82 $GJ/m^3$ | [27] |
| $CuSO_4 \cdot 5H_2O/CuSO_4$ | TGA-DSC | Ms:10 mg T= 25 ºC $p_{H2O}$=13 mbar | Ms:10 mg Trange: 25-150 ºC Heating rate: 1 ºC/min | 1.84 $GJ/m^3$ | 1.85 $GJ/m^3$ | [27] |

Ms: sample mass. RH: relative humidity

## 4. Chemical reactors

When designing a chemical reactor several requirements should be taken into account, mainly: the kinetics of the reaction, mass transfer, heat transfer, safety factors, and economic factors which in many cases the operating expenses may determine the choice of the reactor type and the design method, since operating costs are related to energy input (heating, cooling, pumping, agitation, etc.), energy removal, raw material costs, labour, etc.

A general procedure for reactor design is outlined below [33]:

1. Kinetic and thermodynamic data on the desired reaction is initially collected. These data may be obtained from either laboratory or pilot plant studies.
2. Data on physical properties are required for the design. This may be either estimated or collected from the literature or obtained by laboratory measurements.

3. The rate controlling mechanism which has a predominant role is then identified, for example, kinetic, mass or heat transfer.
4. A suitable reactor type is then chosen, based on experience with similar studies or from the laboratory and pilot plan work.
5. Selection of optimal reaction conditions is initially made in order to obtain the desired yield.
6. The size of the reactor is decided and its performance estimated. Since exact analytical solutions of the design relationship are rarely possible, semiempirical methods based on the analysis of idealized reactors are used.
7. Materials for the construction of the reactor are selected.
8. A preliminary mechanical design for the reactor including the vessel design, heat transfer surfaces, ... is made.
9. The design is optimized and validated.
10. An approximate cost of the proposed and validated design is then calculated.

### 4.1 Chemical reactors classification

The main objective when designing a chemical reactor is to know which volume, type, as well as operating mode are the appropriate for a specific purpose. Within chemical reactors, different criteria can be proposed for classification [34]:

- Number and nature of phases present
    - Single phase
    - Multiple phase or heterogeneous
- The operating mode of the reactor
    - Continuous
    - Semi-batch
    - Batch
- Circulation of phases
    - Countercurrent
    - Concurrent
    - Crosscurrent
- Heat transfer
    - Isothermal
    - Adiabatic

Single phase reactors are the ones that contain one visible phase, usually fluid (liquid or gaseous). Heterogeneous reactions involve a combination of two or more different phases (G/L/S) or two immiscible fluids (L/L).

Continuous, batch, and semi-batch are considered depending on the operating mode. In general, batch reactors operate in non-steady state conditions while continuous are designed for steady state conditions, tubular and stirred tank.

In heterogeneous reactions, each phase can work in one mode, e.g. fixed bed. Possible combinations are: liquid-liquid, gas-solid, liquid-solid, and gas-liquid-solid. When possible it is suggested to analyse the reactors as closer as possible to the ideal reactors. From now on, gas-solid reactors are of interest of this paper, since these are the most of the reactions occurring in TCM for building applications.

### 4.2 Non-catalytic gas-solid reactors

Unlike homogeneous, to deal with heterogeneous reactions there are important requirements to take into account: the modification of kinetic equations due to mass transfer between phases, and the contacting patterns for a two-phase system [35].

Depending on the flow pattern, three main gas-solid technologies are available [34]:

- Fixed bed reactor (also called packed bed): solid particles are arranged in a vessel with the flux of reactants passing through the stationary bed. Heat transfer rates in large diameter packed beds are poor and where high heat transfer rates are required fluidized beds should be considered [36].
- Moving bed: the bed can be removed either continuously or periodically in portions. Fluid circulation is similar to that in a fixed bed.
- Fluidized bed: the solid is present in the form of fine particles that are maintained in suspension by the upward flow of fluid.

Fixed and fluidized bed are close linked since the base from a fluidized bed is a fixed bed, but with the increase of the fluid velocity until the solid particles are suspended but it is not large enough to carry them out of the vessel. A comparison between these three gas-solid reactors is summarized in Table 3.

Here, the aim is to focus on gas-solid reactors, being the solid a non-catalyst, thus taking part of the reaction. Three factors control the design of a fluid-solid reactor; the reaction kinetics for single particles, the size distribution of solids being treated, and the flow patterns of solids and fluid in the reactor. There is a wide choice of contacting methods and equipment for gas-solid non-catalytic reactions. The solution finally adopted may depend very much on the physical condition of the reactants and products. A part of the above mentioned reactors, other types have been developed as rotary reactors [0]. Some of the available reactors for gas-solid reactions are shown in Figure 4.

Table 3. Comparison of G-S reactors

| Reactor | Advantages | Disadvantages | Reference |
| --- | --- | --- | --- |
| Fixed/Packed Bed | Easier for modelling | Low heat and mass transfer<br>High pressure drop | [36,10] |
| Moving Bed | Direct heat transfer between solids and the gas | Complex hydrodynamics | [12] |
| Fluidized Bed | Minimization of the risk of hotspots and thermal instability.<br>Heat transfer coefficients are high | Complex reactor hydrodynamics and modelling.<br>Erosion of internal components | [34] |

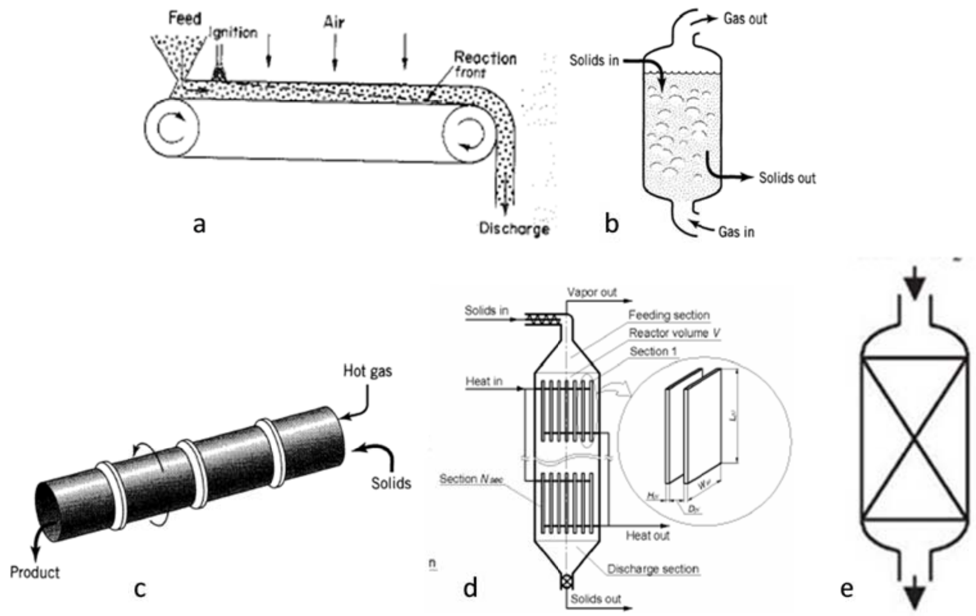


Figure 4. a: moving bed in cross-flow; b: fluidized bed counter-current flow; c: screw or rotary dryer;d: gravity assisted bulk flow; e: fixed bed reactors [35,38 ,39]

## 5. Lab and field test TCM reactors

The available reactors to test TCM and sorption storage under real conditions range from 0.015 to 7850 L. Different configurations and reactors have been designed and tested for results. This information is shown here ordered in time following the year of each publication. This technology is quite new at lab and field test scale (first prototypes around 2000) and still needs further research to improve the overall system to be commercially viable and user attractive.

Within IEA-SHC Task 32 “Advanced storage concepts for solar and low energy buildings”, Subtask B is focused on chemical and sorption storage, where several reports are published about this topic [14, 40].

Monosorp (2004, ITW, Univ. Stuttgart, Germany), is an effective 7.85 $m^3$ open adsorption storage (see Figure 5) integrated in a conventional mechanical ventilation system that has been developed in the Institute of Thermodynamics and Thermal Engineering (ITW), University of Stuttgart and was theoretically and experimentally investigated. The performed adsorption and desorption cycles proved the functioning of the concept and of the system set-up.

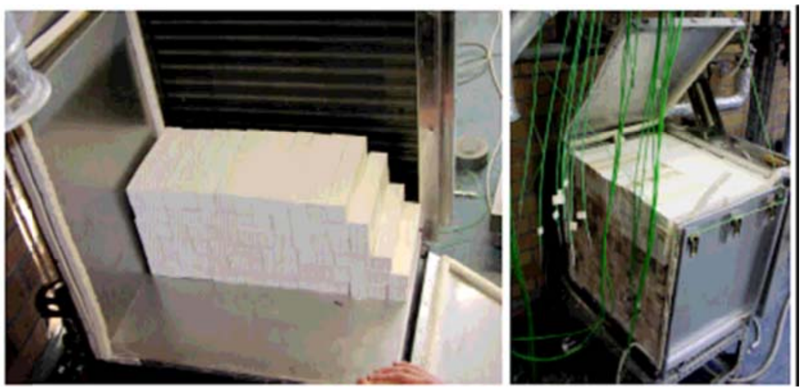

Figure 5. Monosorp prototype [14]

Some of them are developed in the framework of EU or national projects. Modestore (2006, AEE INTEC, Austria), a closed and integrated adsorption heat storage system with the material pair silica gel and water was developed, for use in a single-family house and a first pilot plant was built (see Figure 6) [14]. Experimental results show that the main problem remains on the low storage density due to the adsorption characteristics of the material combination, therefore they are not suitable for an application for heat storage for solar space heating.

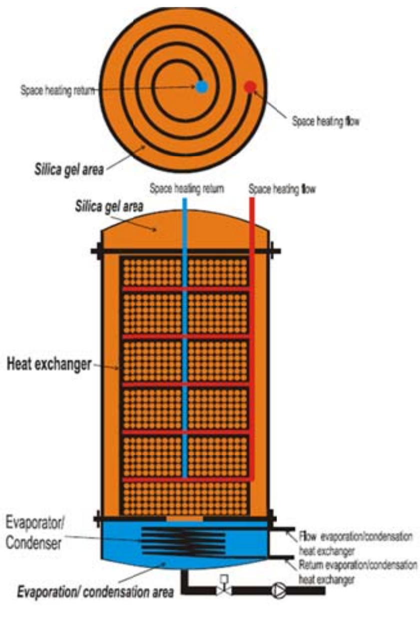


Figure 1. Modestore prototype of a closed and integrated silica gel/water reactor [14]

Zondag et al. 2008 [11] tested the same reactor prototype as in [22], but with zeolites, looking for the influence of the effect of mixing. Results show that stirring strongly increases the heat transport towards the bottom of the tank (Figure 7), the heating of which is shortened from about 8 minutes to 1 minute. Thus, it means an improvement on heat transfer from the powder (TCM) to the heating system.

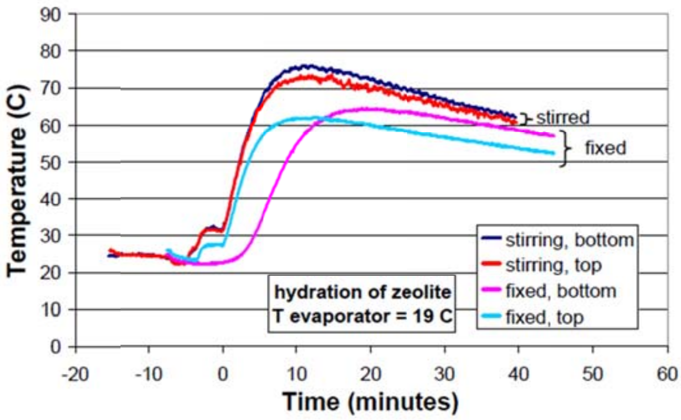


Figure 7. Temperature vs. time curves of the zeolites reactor, with and without stirring it [11]

Mauran et al. 2008 [41] designed a prototype for heating/refreshing a family house based on strontium bromide hydrates ($SrBr_2 \cdot 6H_2O$/ $SrBr_2 \cdot H_2O$) and expanded natural graphite, TCM composite. The modular reactor (Figure 8) of about 1 $m^3$ is able to store, 60 kWh or 40 kWh, for heating and cooling, respectively. Nevertheless, when working, power seems to be lower than expected since heat transfer between composite TCM and heat exchanger is limiting.

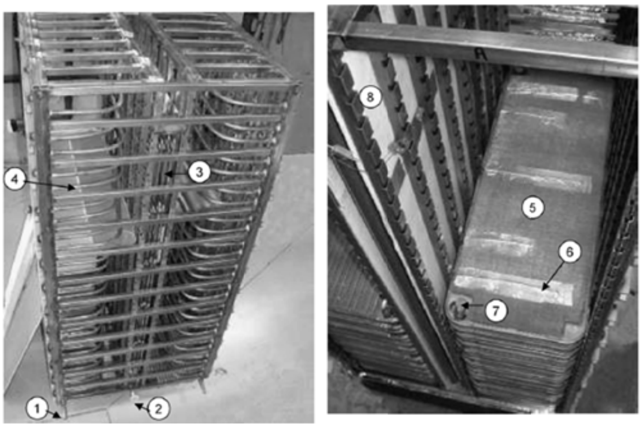

Figure 8. SOLUX modular prototype [41]

Van Essen et al. 2009 [22] built up an experimental setup, based on a 40 g of dehydrated magnesium sulphate ($MgSO_4$), in a 0.015 $dm^3$ fixed bed reactor (see Figure 9), where low pressure conditions, 2.8 mbar, were achieved leading to a better diffusion (compared to previous DSC experiments) of the water vapour to the TCM. Aluminium sulphate, magnesium chloride and magnesium sulphate were also tested. The system is closed (evaporator/condenser) and integrated. Higher temperature lifts are achieved by chlorides. $MgCl_2$ is recommended but it tends to form a gel-like material during hydration.

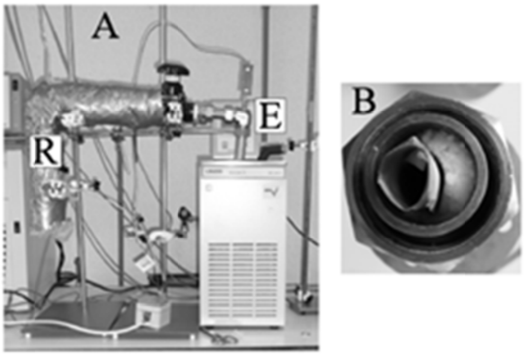


Figure 9. A: Fixed bed setup, where R is the reactor and E denotes for the evaporator. B: detailed zoom of the reactor [22].

Mette and Kerskes et al. 2011 [9, 42] designed a 64 $dm^3$ opened and external reactor as illustrated in Figure 10. The reactor can operate as a moving or fixed bed, which is numerically compared with a salt impregnated zeolite as the TCM. It is concluded that the moving bed in cross flow reactor design is superior to the fixed bed reactor design in terms of the specific thermal energy density released during the reaction. However, the cross flow reactor design has high demands on the reaction control due to the sensitivity of the reaction to a variation in the air inflow conditions. The reactor design is shown in Figure 11. Simulation results show constant power of 400 W.

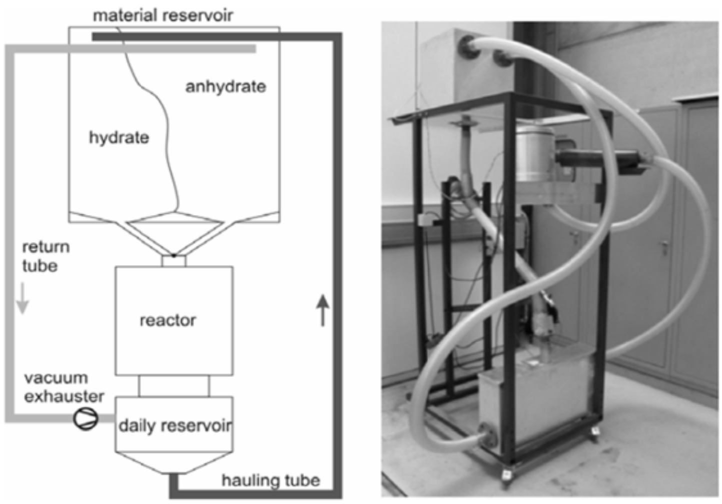


Figure 10. General overview of the system configuration, in external and open configuration [9,42]


Figure 11. Details of the reactor design in cross flow configuration, real picture, and sketch [9,42]

Michel et al. [21] studied how different parameters, such as bed density, binder addition (matrix), gas diffuser, salt grains size, etc. in a fixed bed lab prototype of about 0.8 $dm^3$ affect mass and heat transfer, thus energy density and specific power. A model was also developed based on sharp reaction front and its validation for unidirectional mass transfer. The TCM under study was $SBr_2{\cdot}6H_2O$, achieving energy densities of about 430-460 $kWh/m^3$ for house heating applications. Lab prototype as shown in Figure 12 is two perforated metallic sheets, where the salt is confined, the bed thickness ranges from 40 to 100 mm. The sample holder is a stainless steel tube, 100 mm inner diameter and 467 mm length. This setup is integrated and open configuration.

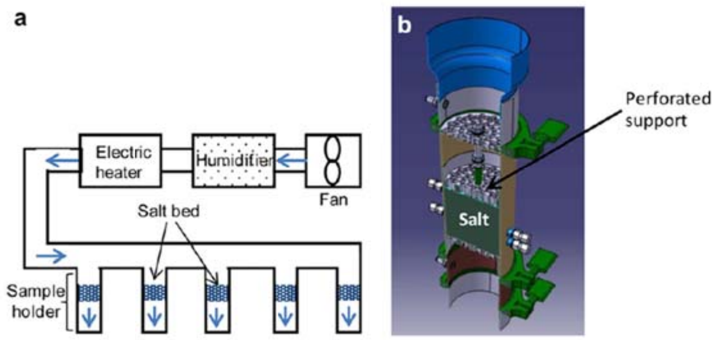


Figure 12. Experimental setup for TCM characterization. A: experimental setup, B: sample holder [21]

Lass-Seyoum et al. [43] developed a closed and integrated reactor. Concretely, they started with a 1.5 L lab reactor, then a 15 L, and finally a 750 L (Figure 13) with two kinds of TCM: zeolites and composites, attalpugite and poolkohl with 30 % $CaCl_2$. With the 15 L two different heat exchangers configurations were tested, applying the best to the 750 L, although some scaling effects were observed. For the 15 L prototype a specific heat storage capacity of about 180-240 Wh/kg was obtained.

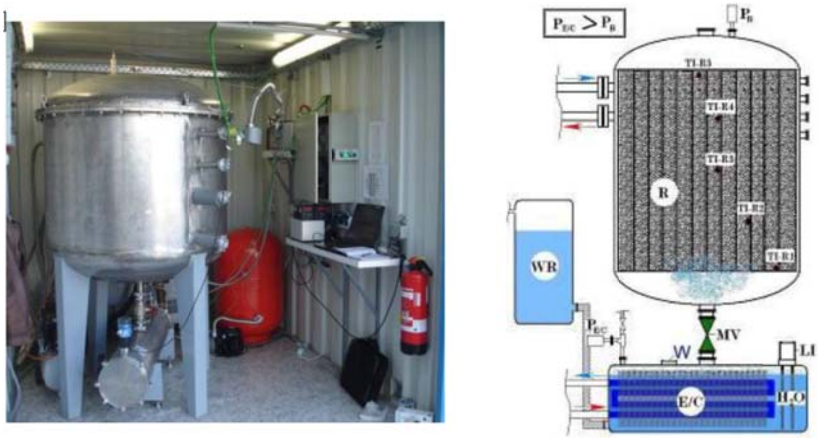


Figure 2. 750 L closed and integrated prototype [43]

Stitou et al. [8] tested closed and integrated barium chloride and ammonia reactor for solar air-conditioning. Two years experimental data show a daily cooling productivity at 4 ºC of about 0.8-1.2 kWh of cold per $m^2$ of flat plate solar collector. The reactor consists in 19 tubes filled with a compressed mixture of 140 kg of anhydrous $BaCl_2$ and 35 kg of expanded natural graphite (Figure 14).

Figure 14. Closed and integrated reactor based on $BaCl_2$ and natural graphite tubes [8]

Cuypers et al. [44] tested two lab-scale vacuum-based zeolite reactors. One reactor is composed by a spiral copper heat exchanger and the other by copper fins with the TCM glued on it (Figure 15). A total energy yield of 60% of the theoretical value was reached with the second setup. Zeolite as TCM was discarded for further prototypes due to economic and technical (needed volume) reasons.

Figure 15. Copper fins with glued zeolites reactor [44]

Zondag et al. [45] built up a 17 $dm^3$ fixed bed lab scale open and integrated reactor with $MgCl_2 \cdot 6H_2O$ obtaining 50 W heating power at 60 ºC. They suggest improvement of heat recovery and pressure drop to increase the performance.

Figure 16. 17 L open and integrated prototype, a) before and b) after insulation [45]

Within European projects of the FP7, SOTHERCO's [46] the major objective is to install, monitor and assess an innovative modular, compact and seasonal thermochemical solar heat-storage system. The modular design, based on the proper arrangement of ~1000L heat-storage modules, is intended to offer the needed flexibility and adaptation to answer the space-heating demand of low-energy buildings, from a single family dwelling up to communities and district heating. MERITS [47] project aim is to build a prototype of a compact rechargeable heat battery based on TCM, for DHW, heating and cooling for single family houses. The prototype is now being built up and will be tested in field in 2015. The COMTES project has as goal to develop and demonstrate three novel systems for compact seasonal storage of solar thermal energy (solid sorption, liquid sorption and supercooling PCM).

Regarding Table 4 first prototypes for building comfort applications were more focused on physisoprtion, mostly zeolites and silica gel, and from 2008 on, salt hydrates and composites based on salt hydrates are preferred.

Table 4. Summary of the reviewed solid-gas thermochemical and sorption storage systems; reactors specifications and main outputs

| | Monosorp U. Stuttgart 2004 | Modestore AEE INTEC 2006 | Zondag 2008 | PROMES 2008 | ECN 2009 | U. Stuttgart 2011 | PROMES U. Perpignan 2012 | Fraunhofer IGB ZeoSys GmbH 2012 | PROMES U. Perpignan 2012 | TNO 2012 | ECN 2013 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Applications | Space heating | Space heating | - | Heating and cooling | Properties characterization | Heating | Mass and heat transfer characterization/ House heating | Heating | Solar air conditioning | - | Heating |
| TCM | Zeolite 4A /Water | Silica gel / water | Zeolites (Köstrolith beads) /Water | $SrBr_2$ + ENG /Water | $MgCl_2$ $CaCl_2$ $AlSO_4$ $MgSO_4$ /Water | Zeolites and Salt impregnated zeolites (9 %wt $MgSO_4$ and 1%wt LiCl) /Water | SBr2·6H2O /Water | Zeolites and composites (attalpugite and poolkohl + 30 % $CaCl_2$) /Water | $BaCl_2$ + ENG /Ammonia | Zeolites/Water | $MgCl_2$ /Water |
| Reactor | n.a. | n.a. | Fixed bed or Stirred | - | Fixed bed | Moving or fixed bed | Fixed bed | - | - | - | Fixed bed |
| Volume (L) | 7850 | 350 (400 kg Silica, 30 kg water) | 0.015 | 1000 | 0.015 | 64 | 0.015 | 1.5, 15 and 750 | 19 tubes of 140 kg of anhydrous $BaCl_2$ and 35 kg of ENG | - | 17 |
| Water vapour pressure (mbar) | - | - | - | 10/60 | 2.8 | 1/20 | 10/18 | 12/42 | - | - | 12 |

| TCM system configuration | Open and integrated | Closed and integrated | Closed and Integrated | Closed and integrated | Closed and Integrated | Open and separated | Open and integrated | Closed and integrated | Closed and integrated | Closed and integrated | Open and integrated |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Conclusions | 12 kWh measured storage capacity | Low storage energy density 13 kWh for heat | Heat transfer inside the reactor is improved when stirring | Stores 60 kW h and 40, for heating and cooling respectively | Higher temperature lifts are achieved by chlorides. $MgCl_2$ is recommended | Simulation results show constant power of 400 W | Energy densities of about 430-460 kWh/m$^3$ | Specific Heat storage capacity ~ 200 Wh/kg. Scaling effects were observed | Daily cooling productivity at 4 ºC of about 0.8-1.2 kWh of cold per m$^2$ of flat plate solar collector | Output power of about 0.6 kW/kg of active material | Effective energy storage density of 0.5 GJ/m$^3$ |
| Reference | 14 | 14 | 11 | 41 | 22 | 9, 42 | 21 | 43 | 8 | 44 | 45 |

Where n.a. stands for not available

## 4. Modelling

Lots of efforts are focusing on simulating thermochemical energy storage overall systems and/or reactors. It is complicated to simulate these systems, especially when storage needs to be included.

An agitated fluidised bed thermochemical reactor system was investigated by Darkwa et al. [48]. The model results showed considerable enhanced adsorption capacities and heat transfer rates. However, in order to promote effective exothermic reaction and heat transfer it is suggested to optimise the thermophysical parameters that affect the minimum fluidising velocity ($u_{mf}$) in the adsorption column.

In [49] it is found that the temperature rise in an open fixed bed system is limited due to the limited thermal mass of air. Furthermore, it is found that reasonable solar fractions can be achieved for the specific system dimensions that are mentioned in the paper. However, the system efficiency is rather low, in the order of 20%. Optimization of the system efficiency can be achieved by control strategy and looking to pressure drop is of importance for the overall coefficient of performance (COP) of the system.

In [21] how a solid/gas reaction, of a seasonal thermochemical storage process, in a fixed bed performs is shown. The model is based on the assumption of a sharp reaction front moving through the bed during the reaction, and, separating the reacted and unreacted parts of the bed. The comparison between the model and experimental results validates the sharp reaction front model. It demonstrates that this tool is simple and very efficient to predict the transformation of high density porous reactive beds, as long as the assumption of unidirectional mass transfer is respected.

An open and integrated reactor based on $SrBr_2$ was modelled focusing on the hydration reaction, which is more problematic [50]. Parametric studies are carried out to evaluate the influence of some parameters on the performance of different system configuration, pointing out external conditions, components performances and salt characteristics influence on the COP and productivity rate.

Balasubramanian et al. [51] developed a mathematical model when charging for salt hydrates. Results show that the process performance is improved by introducing a smaller heat flux and considering materials that have larger thermal conductivities, higher specific heat capacities, and lower thermochemical desorption rates.

Energy and exergy analyses of a closed thermochemical system are performed in [52]. General efficiency expressions are determined for the three involved processes: charging, storage, and discharging, as well as for the overall system.

A method combining constructal approach and exergy analysis is presented in [53], to optimize (shape) a gas/solid high temperature thermochemical reactor. There storage time is also taken into account, and expressed according to the design parameters.

Pal et al [54] present a material-independent model that can be used to simulate an open flow adsorption and desorption process.

## 5. Conclusions

TGA-DSC coupled lab techniques are being used to characterize TCM. This way could be useful for a first material selection or screening. However, to properly characterize TCM and for the further reactor design, TCM should be characterized in a lab scale reactor.

Most of the prototypes nowadays being tested do not achieve the expected storage capacity. In addition all of the storage systems have irreversibility in the process themselves during charge and discharge resulting in lower store efficiencies. From the material side, mass transfer is limiting due to compaction of salt hydrates and thus the impediment of water vapour diffusion. One of the possible solutions is to add a matrix material (inert or adsorbent), but it is not always an improvement since sometimes leads to a decrease in kinetics.

Furthermore, experimental kinetic data, modelling (coupling kinetic, heat and mass transfer equations) and validation (lab scale, pilot plant scale) are essential steps to make TCM technologies available and market competitive.

From the literature review, first prototypes for building comfort applications were more focused on physisorption, mostly zeolites and silica gel, and from 2008 on, salt hydrates and composites based on salt hydrates are preferred.

Several prototypes are being designed and tested. Most of the experimentally tested prototypes are still at lab scale, despite some of them are currently being tested at real houses. Within the TCM reactor configurations, fixed bed is the most common. Open and closed, integrated and non-integrated systems configurations have been tested. Prototypes volume values vary from 0.015 to 785 $dm^3$. Nevertheless, chemical engineering fundamentals bank on fluidized beds, moving beds or rotary kiln reactors to enhance heat transfer.

A part of the gas-solid reactor choice, several modifications can be made always looking for promoting mass and heat transfer; for instance increase the contact surface area between solid and gas or add gas diffusers.

It is always a compromise; there is not the unique and best solution.

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