

## THERMOCHEMICAL SOLID/GAS PROCESS FOR LONG TERM STORAGE OF THERMAL ENERGY

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### ABSTRACT

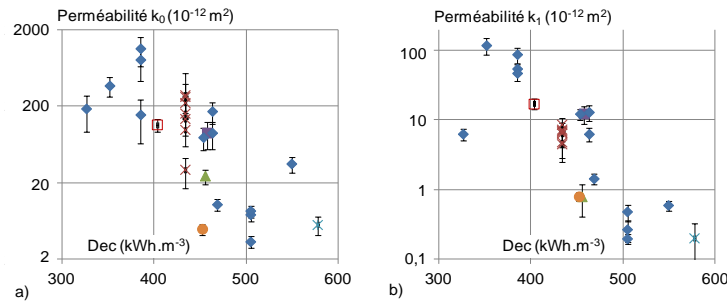
The use of solar energy for household applications is a relevant mean to reach the Kyoto objectives. To maximize this use of solar energy for heating, it can be interesting to store solar energy in summer, thanks to a long-term storage process (3-6 months) and use it for the following winter period. Several studies deal with seasonal storage for residential applications [1]. Among available processes, a thermochemical storage takes advantage of a high storage density (about 200 to 500 kWh.m<sup>-3</sup>), and negligible heat losses between the storage and the recovery periods because the energy is stored as chemical potential and the sensible heat of the elements is weak. Therefore, this kind of storage is relevant for seasonal storage for house heating. As a matter of comparison, the energy density of latent storage is about 90 kWh.m<sup>-3</sup> and the energy density of sensible water is about 54 kWh.m<sup>-3</sup> (for a  $\Delta T$  of 70 °C and heat losses of 25%). However, up to date, no solid/gas thermochemical seasonal storage system has been completed.

Such thermochemical storage process involves a reversible chemical reaction between a solid and a gas. For safety reasons for its use in housing, the reactive gas is steam, and a well known hydrate/water pair has been chosen (SrBr<sub>2</sub>/H<sub>2</sub>O) [2]. The dehydration is the storage step (using solar heat input) and the hydration is the heating step (winter). Most of thermochemical systems operate as closed system with pure steam, but the feasibility of open systems running with moist air is currently investigated [3]. We have chosen this working mode that leads to simpler and cheaper reactors.

Beside the high energy density criteria, a seasonal storage system has also to reach a given thermal power production during the heat recovery step to fit the heating demand. Thus, the key point of such a thermochemical process is the design of the reactive porous bed. It must take into account two antagonistic features: mass and heat transfer within the porous solid reactant, and energy density of the reactive bed. Indeed, enhancing the apparent energy density of the final prototype can only be performed by reducing the bed porosity and the volumes for mass diffusers, but that could result in mass transfer limitation for the reactive gas and consequently in a strong decrease of the thermal power released by the storage system. Therefore, it is essential to characterize mass transfer in the reactive porous and its evolution according to the bed density.

Experimentation has been carried out in order to characterize the mass transfer and the reaction kinetics of the porous bed of reactive salt. The operating principle of the apparatus is based on the measurement of the pressure drop across the porous fixed bed and the flowrate of moist air (at controlled humidity and temperature passing through it). That allows deducing the porous bed permeability according to Darcy law. The kinetics is deduced from the weight variation of the sample. Several samples with different implementation parameters (density, porosity, mass ratio of binder, diffuser, porosity and grain size) have been tested [4]. The following figures summarize the permeabilities of reactive beds according to their

energy density (Dec, kWh of energy stored / m<sup>3</sup> of porous bed), in a range from 300 to 600 kWh/m<sup>3</sup>. Permeabilities are measured at the boundaries of the reaction (X=0 i.e. SrBr<sub>2</sub>.1H<sub>2</sub>O, and X=1 i.e. SrBr<sub>2</sub>.6H<sub>2</sub>O).



Perméabilities of salt beds vs. Energy density Dec. a)  $k_0$  (dehydrated bed), and b)  $k_1$  (hydrated bed). Points at the same Dec correspond to several reaction cycles of the same sample.

These figures exhibit a strong decrease of the permeability vs the bed density. The permeability changes by three orders of magnitude when the energy density ranges from 300 to 600 kWh.m<sup>-3</sup>, i.e. in the targeted range for long term storage application. Moreover, the permeability also strongly changes during the reaction: it decreases by more than one order of magnitude. Thus, the density of the bed has a very strong impact on mass transfer and the bed has to be carefully implemented to avoid mass transfer limitation.

The variation of permeability during the reaction has been carefully investigated for a sample at Dec=433 kWh.m<sup>-3</sup>. Seven successive reaction cycles have been carried out. Permeability becomes quite stable after the third cycle. Regarding the hydration step, this experimentation shows that permeabilities do not evolve linearly but following a 1/X function. This variation can be explained assuming a reaction front in the reactive bed, which moves in the same direction as the moist air flow. This front separates a fully reacted layer and an unreacted layer. Thus, the overall permeability of a bed, at the reaction advancement X, is a combination of that of two layers in series, one at  $k_1$  and the second at  $k_0$ ; the thickness of each layer is respectively X and (1-X). As a result, the equivalent permeability of the bed is expressed as:  $k_{eq}(X) = 1/[(X/k_1)+(1-X)/k_0]$ . Conversely, during the dehydration step, the experimentation demonstrates that the permeability evolves linearly:  $k_{eq}(X) = k_1.X+k_0.(1-X)$ . That could be explained by diffusion path through the layer created by the dehydration. These evolutions of permeability have to be taken into account for the dimensioning of the reactor.

Finally, a 2D model combining heat and mass transfer and kinetics has been developed and used to analyze the limitation of the reaction. A sensitivity study was carried out, for these three phenomena. Thus, mass transfer is clearly the most limiting phenomena, in the range of parameters investigated. And this limitation is very strong at the end of hydration and can lead to uncompleted reaction. Thus the permeability  $k_1$  of the SrBr<sub>2</sub>.6H<sub>2</sub>O bed is the main parameter to take into account when dimensioning the reactive bed and reactor.

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