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# CONSTRUCTAL OPEN REACTORS FOR THERMOCHEMICAL ENERGY STORAGE

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#### ABSTRACT

This work documents the study of two concepts of open reactors for thermochemical energy storage. While classical thermal storage uses sensible or latent heat to store thermal energy, thermochemical energy storage uses an endothermic / exothermic chemical reaction. The process studied is based on the hydration and dehydration of a reactive salt by a flow of moist air in order to release and store heat respectively. The first concept studied is a storage module composed by the pattern "one salt bed surrounded by an inlet and an outlet channel, placed in parallel". The second concept is a storage module made of by tubes impregnated with the reactive salt on their intern face. In this configuration, the tubes and the impregnated salt layer length scales are in the order of micrometer. Both concepts are presented using the Constructal law of design.

In the first concept, air flows through the salt bed, corresponding to a forced convection through porous media problem, whereas in the second concept the air flow licks the impregnated salt and the chemical reaction occurs within the salt thanks to diffusion only.

The analytical part is based on the Constructal law approach. From the main trends in terms of pressures distribution the geometrical features are deduced to obtain the design of compact and thermally efficient systems.

Next, the discovered trends are backed up with numerical experiments. The geometrical dimensions are morphed with the purpose to move towards better performances. A ratio  $\beta$  between the heat produced by the chemical reaction within the entire module and the overall pumping power necessary to blow the fluid is determined to compare the configurations of each concepts.

In accord with Constructal design, the number of salt beds in the first concept is morphed to reach equipartition of imperfections. The results show that with this evolution, the ratio  $\beta$  increases. In the second concept, the salt volume must be allocated in such a way that the time for water vapor diffusion through the salt matches the time for hydration / dehydration.

#### INTRODUCTION

The use of renewable energy is restrained by the mismatch between energy production and consumption periods. For example, using solar energy for heating in building applications is a valuable solution provided long term storage (seasonal scale) can be achieved. In addition, classical thermal energy storage, sensible and latent, means energy leakage along the storage period. These problematics led to an increase in the interest for thermochemical energy storage: in this case the thermal energy is stored or released via a chemical reaction. This reaction involves a salt and its hydrate, and the energy released comes from the latent enthalpy and the bonds dissociation enthalpy during the hydration and dehydration processes. The reaction is typically summarized by:

#### $Hydrate(s) + heat \leftrightarrow Deshydrate(s) + H_2O(vapor)$

Thermochemical energy storage is subdivided into two types: open and closed. This work focuses on processes involving open systems. In an open system the fluid used to hydrate the salt is carried coming from the external environment and blown through or along the salt.

The open system reactor is considered through two different configurations. In the first concept the salt is divided into salt layers surrounded by an inlet and an outlet channel, in parallel. The layers are assimilated to porous media through which the air flows. The water vapor needed in the reaction is transported via forced convection. The problem is at macro scale (centimeter). In the second concept the reactive salt is impregnated on the inner wall of cylindrical channels, and the module is fulfilled with these tubes. The air flow licks the impregnated salt and the chemical reaction occurs within the salt thanks to diffusion only. In this configuration, the tubes which compose the storage module are of the order of micrometer.

# NOMENCLATURE

Symbols		
а	reaction advancement	
Α	surface, m <sup>2</sup>	
С	concentration, mol/m <sup>3</sup>	
Ср,	specific heat capacity, J/(kg K)	
D	channel thickness, m	
D <sub>h</sub>	hydraulic diameter, m	
$D_{v}$	diffusion coefficient of water vapor in air,	
	m²/s	
f	friction factor	
Н	height, m	
Δh	enthalpy of reaction, J/mol	
К	salt permeability, m <sup>2</sup>	
k	thermal conductivity, W/(m K)	
k <sub>cin</sub>	kinetic reaction constant, 1/s	
<i>k</i> <sub>st</sub>	stoichiometric coefficient of the reaction	
L	length, m	
ṁ	mass flow rate, kg/s	
$M_{\nu}$	molar mass of vapor, kg/mol	
n	number of salt layers and channels	
ns	bulk molar density, mol/m <sup>3</sup>	
p	pressure, Pa	
$\rho_v$	partial water vapor pressure, Pa	
R	tube radius, m	
Re	Reynolds number	
Т	temperature, K	
t	time, s	
U	average fluid velocity, x axis, m/s	
u	velocity vector, m/s	
V	average fluid velocity, y axis, m/s	
ν	volume, m³	
x,y,z,r	coordinates, m	
W	module width, m	

## Greek symbols

α	thermal diffusivity, m²/s
β	ratio of heat released and pumping power
ε	salt porosity
μ	dynamic viscosity, Pa.s
V	kinematic viscosity, m²/s
ρ	density, kg/m <sup>3</sup>
$\Phi$	module apparent porosity

Subscripts	
eff	effective
i	internal
in	inlet
max	maximum
salt	salt

#### I. NUMERICAL MODEL AND VALIDATION

In order to study the two thermochemical open reactor concepts, we developed a numerical model describing heat and mass transfers.

In the model, mass conservation for the water vapor (Eq. 1) and for humid air (Eq. 2) are solved in the channels (exit and entrance). The air flow in the channels is laminar (Eq. 3). To complete the set of equations in the channels, the energy conservation is written (Eq. 4).

$$\frac{Dc}{Dt} + \nabla (-D_{\nu} \nabla c) = 0 \tag{1}$$

$$\frac{D\rho}{Dt} = 0 \tag{2}$$

$$\rho \frac{D\boldsymbol{u}}{Dt} = -\boldsymbol{\nabla}p + \mu \boldsymbol{\nabla}^2 \boldsymbol{u} \tag{3}$$

$$\rho c_p \frac{DT}{Dt} + \boldsymbol{\nabla} \cdot (k \boldsymbol{\nabla} T) = 0 \tag{4}$$

where *c* is the water vapor concentration, and  $D_v$  is the vapor diffusion coefficient. where  $\rho$  is the humid air density.

where **u** is the velocity vector and *p* the pressure.

Mass conservation for the water vapor and for humid air is also solved in the salt. The term in the right hand side of Eqs. 5 and 6 accounts for the source/sink due to the salt dehydration/hydration. To couple with the Navier-Stokes equations used in the channels, the Brinkman equation (Eq. 7) is used, describing the momentum conservation. Here the salt porosity  $\varepsilon$  is high enough to justify the use of the Brinkman equation. The energy conservation is written with a heat source/sink created by the chemical reaction in the salt (Eq. 8).

$$\varepsilon \frac{\partial c}{\partial t} + \nabla \left( -D_{v,eff} \nabla c \right) + u \nabla c = -k_{st} n_s \frac{da}{dt}$$
(5)

$$\varepsilon \frac{\partial \rho}{\partial t} + \nabla(\rho \boldsymbol{u}) = -k_{st} n_s \frac{da}{dt} M_v \tag{6}$$

where  $D_{v,eff}$  is the effective diffusion coefficient of the water vapor in the air inside the porous medium, and  $M_v$  is the molar mass of vapor.

$$\rho \frac{D\boldsymbol{u}}{Dt} = \varepsilon \left[ -\boldsymbol{\nabla} p + \mu \boldsymbol{\nabla}^2 \boldsymbol{u} + \frac{\mu}{K} \boldsymbol{u} \right]$$
(7)

$$\left(\rho c_{p}\right)_{eff}\frac{\partial T}{\partial t}+\rho c_{p}\boldsymbol{u}\cdot\boldsymbol{\nabla}T+\boldsymbol{\nabla}\cdot\left(k_{eff}\boldsymbol{\nabla}T\right)=n_{s}\frac{da}{dt}\Delta h$$
(8)

where  $(\rho c_p)_{eff}$  and  $k_{eff}$  are given by where  $c_s$  is the heat capacity of the salt.

$$(\rho c_p)_{eff} = (1 - \varepsilon)\rho_{salt}c_s + \varepsilon\rho c_p$$
 (9)

The reaction advancement rate da/dt is given by:

$$\frac{da}{dt} = k_{cin} \left( 1 - \frac{p_{eq}}{p_v} \right) (1 - a) \tag{10}$$

Note that the water vapor transport is written within the entire domain because it must be expressed in the salt to determine the mass source/sink for the chemical reaction.

The temperature  $T_{in}$  and the water vapor concentration  $c_{in}$  are fixed at the fluid entrance. To assume a fully developed flow at the inlet, an entrance length greater than 0.05 Re D<sub>h</sub> is imposed [1], for an inlet mass flow rate  $\dot{m}$ . The atmospheric pressure is applied at the outlet for the fluid and an outflow condition is applied as a boundary condition for the heat transfer. The transport of water is described with similar boundary conditions. The following conditions are used for all the other external boundaries: thermal insulation, no-slip velocity, and zero vapor flux.

The fluid is at rest and at atmospheric pressure at t = 0, the entire initial temperature of the system is  $T_0$ . The vapor concentration is  $c_0$  corresponding to the equilibrium vapor pressure at temperature  $T_0$ .

A finite element software is used to solve the equations system [2]. The model meshing was optimized in a dedicated study where the energy and mass conversation were used as verification criteria.

The numerical results produced with the model are compared to experimental data obtained in the literature [3], corresponding to several cycles of hydration and dehydration, under different conditions. We observe that the experimental results and the numerical ones match very well (see Fig. 1), validating the model. All the model and experimental characteristics are in Ref. [4].



Fig. 1: Reaction advancement as a function of time, for 3 cycles of hydration-dehydration, comparison with experimental results.

# II. 1<sup>ST</sup> CONCEPT: PARALLEL SALT BED

Here a fixed module volume  $\mathcal{V} = nWLH$  and a fixed volume of salt are considered. The salt volume is expressed by  $\mathcal{V}_{salt} = n WLH_{salt}$  which gives an apparent porosity  $\Phi = 1 - n H_{salt}/H$  for the storage module. In this work, the apparent porosity is 20%. Humid air is blown along the channels and exits in the opposite direction after crossing each salt bed. The storage module is presented in Fig. 2. In a heating mode, water vapor molecules react with the salt, resulting in heat released to the air which is consequently less humid after leaving the reactor.



Fig. 2: Sketch of the thermochemical energy storage module, with 2 salt beds.

We begin the work on the first concept by an analytical approach based on the Constructal Law of design [5]. Looking for equipartition in the distribution of the imperfection, we consider here the pressure losses along the channels and pressure losses through the salt, as a porous medium. We write:

$$\Delta P_{channel} \sim \Delta P_{Hsalt} \tag{11}$$

From  $p(x) = f \frac{1}{2} \rho U^2 \frac{4dx}{D_h}$  we calculate  $\Delta P_{channel}$  [4]:

$$\Delta P_{channel} = \frac{12\nu(D^2 + W^2)}{A^3} \dot{m} \frac{L}{2}$$
(12)

while  $\Delta P_{Hsalt}$  can be estimated from  $\dot{q} = \frac{\dot{m}}{2}(T_{out} - T_{in})$ , where the mass flow rate is given by  $\frac{\dot{m}}{2} = \rho VWL$ . Assuming a Darcy flow through the porous medium, we have  $\Delta P_{Hsalt} = \frac{\kappa}{\mu} \frac{V}{H_{salt}}$ , where  $\kappa$  is the salt permeability. Equation 11 becomes:

$$12K \sim \frac{\phi^3 (1-\phi) H^4 \mathcal{V}^2}{n^2 L^2 [(\phi L H^2)^2 + (n\mathcal{V})^2]}$$
(13)

Equation 13 is plotted in Fig. 3, as a function of *n*, the number of salt beds. The configuration reaches equipartition of the imperfection when *n* increases. The difference between the two terms starts vanishing when the module contains 10 salt beds.



Fig. 3: The two terms of Eq. 13 as a function of *n*.

Then numerical experiments were run to confirm the previously discovered trends. The module dimensions *H*, *W* and *L* are fixed (*H* = 12.5 cm, *W* = 10 cm and *L* = 8 cm), while the number of salt layer varies. Hence the salt slabs thickness, the number and thickness of the air channels change too. The total mass flow rate, the inlet temperature and the inlet relative vapor pressure of the humid air are kept constant ( $\dot{m}_{total} = 0.89 \text{ m}^3/\text{h}$ ,  $T_{in} = 25^\circ\text{C}$ ,  $p_{v,in} = 997.5 \text{ Pa}$ ).

The ratio between the heat released by the chemical reaction within the entire module and the overall pumping power necessary to blow the fluid through the module,  $\beta$ , is shown in Fig. 4, as a function of the non-dimensional time  $\tilde{t} = t/t_{max}$ , where  $t_{max}$  is the time for an advancement a = 1.



Fig. 4: Ratio β, as a function of non-dimensional time

The figure highlights the impact of the salt number on the energetic performance of the module: when the number of salt layer increases, the ratio  $\beta$  increases too.

Next, degrees of freedom are added in the design of the module: the lengths *H*, *L* (so *W*) are allowed to vary while the volume and the module porosity remain fixed. Figure 5 exhibits the ratio  $\beta$  as a function of the shape ratio *H/W* for different number of salt beds.



Fig. 5: Ratio of heat released and pumping power,  $\beta$ , as a function of *H/W* for different numbers of salt layers.

Figure 5 shows that a significant difference in the energetic performance exists between the different cases tested, depending on the number of salt beds. When the aspect ratio of the reactor is fixed, the ratio  $\beta$  increases with the number of salt layers. Furthermore the shape of the reactor module has impact on the results as seen on the results corresponding to 10 salt layers.

### III. 2<sup>ND</sup> CONCEPT: IMPREGNATED TUBE

In the second concept a cylindrical tube is considered. The cylinder has a radius R and a length L, the salt is deposited uniformly along the internal wall. The salt volume is expressed by  $\mathcal{V}_{salt} = \pi L(R^2 - R_i^2)$  where  $R_i$  is the inner radius. Moist air enters from one end of the tube and leaves the channels on the opposite side. Assume that the salt impregnation on the internal tube wall is done at grain scale. The heat transfer fluid licks the salt, water vapor diffuses within, allowing the chemical reaction to happen, and heat to be stored or released.



Fig. 6: Sketch of 1 element of the thermochemical energy storage module.

Note that, in order to correspond to the problem new physics, the model equations are adapted: in the salt layer water vapor molecule are carried by pure diffusion through the salt grains. Therefore only mass conservation for vapor is solved at salt level and the intra diffusion coefficient is taken to 1.2 10<sup>-13</sup> m<sup>2</sup>/s [6]. Equally the energy conservation at the salt level becomes:

$$c_{p_{salt}} \frac{\partial T}{\partial t} + \boldsymbol{\nabla} \cdot (k_{salt} \boldsymbol{\nabla} T) = n_s \frac{da}{dt} \Delta h \tag{14}$$

The channel length is maintained constant (1cm). The inlet mass flow rate, temperature and relative vapor pressure of the humid air are also fixed. We are interested in the impact of the radius ratio on the reaction advancement. In Fig. 6 the radius ratio varies between 0.73 and 0.93. Here the inner radius is fixed (140  $\mu$ m), while the salt thickness changes (from 10 to 53  $\mu$ m). Figure 7 presents the reaction advancement after 100h. The reaction advancement is higher when increasing the radius ratio *R<sub>i</sub>/R*. When *R<sub>i</sub>* is fixed, increasing the radius ratio means to decrease the salt volume. This is a counter-intuitive result that indicates how to allocate the salt volume. As the process is controlled by mass diffusion through the salt, the thinner the salt layer, for a given inner radius, the higher the reaction rate.

Next, the salt volume is kept constant together with the cylinder length (L=1cm). The radius ratio changes from 0.88 to 0.98, which means that channel inner and outer radius,  $R_i$  and R, therefore vary respectively between 70 – 210 µm and 80 – 213.5 µm. The reaction advancement (after 100h) is plotted as a function of the ratio  $R_i/R$ , see Fig. 8. Once again, the reaction advancement is higher when increasing the radius ratio  $R_i/R$ . For a constant tube length the salt volume should be allocated in such a way that the radius ratio is the closest to 1.



Fig. 7: Reaction advancement at t = 100h, as a function of  $R_i/R$ , for different cases with the same fluid volume.



Fig. 8: Reaction advancement at t = 100h, as a function of  $R_i/R$ , for the same salt volume.

We show in Fig. 9 the reaction advancement in time for 2 values of the radius ratio and 2 different inlet conditions. The thick lines correspond to a fixed mass flow rate, while the dotted lines were obtained by setting the inlet mass flow rate to zero in order to consider pure diffusion of vapor molecules along the channel. The latter result therefore correspond to the lowest advancement curves that might be obtained for each configuration. For the highest radius ratio imposing an inlet mass flow does not have a significant impact on the reaction advancement, which ends almost at the same time. Results are different in the case of a smaller radius ratio because the salt thickness is bigger. Therefore the diffusion time along the channel tends to delay the advancement of the reaction through the salt.



Fig. 9: Reaction advancement as a function of time, for 2 values of the radius ratio and 2 different inlet conditions.

#### CONCLUSION

In this work we showed that an efficient thermochemical energy storage can be achieved by working on the geometrical configuration. When the salt is placed in parallel layers through which humid air is blown, increasing the number of layers for a fixed apparent volume and fixed porosity allows to improve the energy performance as predicted by the Constructal law: the optimal distribution of imperfection concept helps predicting what the number of salt layers should be. In addition increasing the compactness of the module increases also the energetic performance. In configurations where the fluid leaches the salt by being blown through a tube impregnated with salt, results indicate that the salt volume can be allocated in such a way that water vapor diffusion is facilitated, leading to faster reaction advancements.

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