Seasonal Storage of Solar Heat

Reactor Modeling

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ABSTRACT

This work is aimed to illustrate the formulation and implementation of a thermo-chemical reactor model for seasonal storage of solar heat under development at the Energy Research Center of the Netherlands, in such a way to give information about the design of the planned lab-reactor upscale. The implementation of the model has been carried out by using the commercial software COMSOL Multiphysics, which enabled to solve the proposed system of partial differential and algebraic equations, both in space and time.

1. INTRODUCTION

Thermal energy storage is an important technology for renewable energy systems and energy efficiency. By improving the effectiveness of thermal storage, the effectiveness of all renewable energy technologies that supply heat can be improved.

Particularly for solar thermal systems, thermal energy storage is essential. To reach high solar fractions, it is necessary to store heat (or cold) efficiently for longer periods of time. Until now, no cost-effective compact storage technologies are available to do this. For high solar fraction systems, hot water stores are expensive and require very large volumes. They also have significant heat losses when used in long term storages.

An alternative storage technology is based on the use of thermo-chemical materials (TCMs). This technology is now only available on a laboratory scale. Further research and development is needed before these technologies can be developed into commercial solutions.

A thermo-chemical material can store thermal energy in the reversible breaking and restoring of the chemical binding of two molecules

$$AB + Heat \rightleftharpoons A + B \,.$$
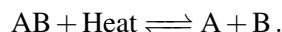
This chemical bond has a higher energy density than heat stored as sensible heat (e.g. hot water storage) or heat stored in a phase change (e.g. ice storage). In addition, the energy can be stored in a TCM for a very long time without any loss of the stored energy of the chemical binding.

From a materials inventory study, a number of interesting TCMs were identified, including magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) as one of the most promising materials for seasonal heat storage (Zondag et al. (2010)).

The following reactions apply for this TCM

$$MgCl_2 \cdot 6H_2O \rightleftharpoons MgCl_2 \cdot 4H_2O + 2H_2O(g) \,,$$

$$MgCl_2 \cdot 4H_2O \rightleftharpoons MgCl_2 \cdot 2H_2O + 2H_2O(g) \,.$$

In order to study the applicability of the $MgCl_2 - H_2O$ system, several experiments have been performed on small lab-scale thermo-chemical heat storage system. The heat storage system contains a reactor where the absorption and desorption of water vapour on MgCl2 is carried out. An open atmospheric reactor is applied in the lab-scale systems because of its simplicity and potential low costs. Air, with its water vapour content, flows through the reactor and depending on the air temperature and humidity level the sorption reactions will take place.

In order to further analyze the performance and develop the technology for seasonal heat storage application, upscaling of the small test reactor towards a full system is needed.

The aim of this work is the formulation and implementation of a mathematical model for the thermochemical reactor under development at ECN, in such a way to give information about the design of the upscaled reactor. The implementation of the model is carried out by using the commercial software *COMSOL Multiphysics* that enables to solve the proposed system of partial differential equations, both in space and time.

2. REACTOR MODEL

The reactor analyzed is made up of a porous bed in which both a solid and a gas phases are present, as shown in Fig. 1. The solid matrix is assumed rigid. The interconnectedness of the void (the pores) allows the air flow through the material. In a natural porous medium, since the distribution of pores is irregular, on the pore scale (the microscopic scale) the flow quantities (velocity, pressure, etc.) will be irregular. However in typical experiments the quantities of interest are measured over areas that cross many pores and such space-averaged (macroscopic) quantities change in a regular manner with respect to space and time. The approach adopted in this work is based on macroscopic equations obtained by averaging over an opportune volume containing many pores. The equations are derived with variables averaged over a sufficiently large representative elementary volume (REV), as shown in Fig. 1.
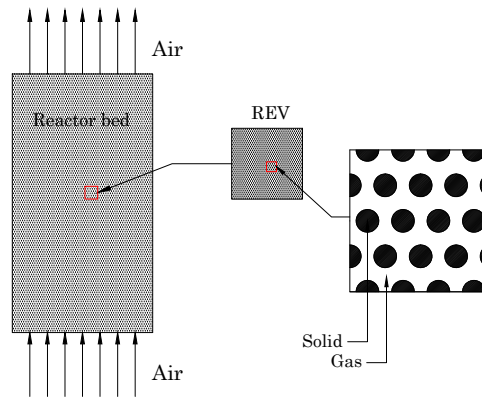

Figure 1: *Reactor scheme and REV.*

In order to develop the mathematical model, the following assumptions are considered

- Constant air density.
- Constant conductivity for gas and solid phases.
- No diffusivity between gas and solid.
- Negligible natural convective heat transfer.
- No friction term in the energy balance.
- Negligible mass transfer resistance in the air side.
- Darcy's formulation for the pressure drop in the porous bed.
- Constant inlet velocity vector. Vector oriented in the longitudinal direction.
- Negligible radiation.

2.1 Conservation equations

In this subsection the conservation equations, derived for the reactor model, are presented.

Mass balance Due to the chemical reaction between the water in the air and the salt in the bed, water vapor mass fraction will change while passing in the reactor bed. The mass fraction of the water vapor in the air is defined as $\xi_w = \frac{m_w}{m_w + m_{da}}$. For the water vapor, the mass conservation is, considering ρ_f constant and neglecting the bed diffusion,

$$\varepsilon \rho_f \frac{\partial \xi_w}{\partial t} + \rho_f (\mathbf{u} \cdot \nabla) \xi_w = r_w \,, \tag{1}$$

where r_w [$kg_{\text{water}}/m^3 s$] is the reaction rate of absorption of water in the bed and the velocity vector $\mathbf{u}$ is defined as $\mathbf{u} = (u, v)$. For the solid

$$(1-\varepsilon)\frac{\partial \rho_s}{\partial t} = -r_w \,, \tag{2}$$

in which the convection term is not present since the solid is considered steady.

Momentum balance   In the reactor model, the momentum balance is based on Darcy's law

$$u = \frac{K}{\mu}\frac{P}{x}, \tag{3}$$

with K the specific permeability or intrinsic permeability. In vector form

$$\mathbf{u} = \mu^{-1}\mathbf{K}\cdot\nabla P \,, \tag{4}$$

in which $\mathbf{K}$ is, in general, a second-order tensor. Under the assumption of isotropic medium

$$\nabla P = -\frac{\mu}{K}\mathbf{u} \,. \tag{5}$$

As reported by Dullien (1992) the hydraulic radius theory of Carman-Kozeny leads to the relationship

$$K = \frac{\varepsilon^3 d_p^2}{180(1-\varepsilon)^2} \,. \tag{6}$$

that gives satisfactory results for media that consist of particles of approximately spherical shape and whose diameters fall within a narrow range.

Darcy's equation is valid in the range of low fluid velocities ($Re < 1$). At high velocity (but still in laminar regime) an expression that is linear in $\mathbf{u}$ is not sufficient, since the form drag due to the solid obstacles becomes of the same order of magnitude of the friction drag. As reported by Nield and Bejan (2006), Forchheimer's equation has been found to be a reliable modification to Darcy's equation as

$$\nabla P = -\frac{\mu}{K}\mathbf{u} - c_F K^{-1/2}\rho_f|\mathbf{u}|\mathbf{u} \,, \tag{7}$$

where c_F is a dimensionless form-drag constant.

An expression for c_F is given by Beavers et al. (1973)

$$c_F = 0.55\left(1 - 5.5\frac{d_p}{D_e}\right) \,, \tag{8}$$

with the equivalent diameter of the bed

$$D_e = \frac{2wh}{w+h} \,, \tag{9}$$

defined in terms of the height h and width w of the bed.

Energy balance   Considering an isotropic medium, negligible viscous dissipation and constant fluid density, the energy balance is given by

$$\rho C_P \frac{DT}{Dt} = k\nabla^2 T + q^{'''} \,, \tag{10}$$

in which k, ρ and C_P are considered constant in time (although C_P is dependent from the temperature and the hydration). From the definition of the material derivative, assuming that the surface porosity is equal to the porosity, for the solid phase the energy balance becomes

$$(1-\varepsilon)\rho_s C_s \frac{\partial T_s}{\partial t} = (1-\varepsilon)k_s\nabla^2 T_s + q_s^{'''} \,, \tag{11}$$

and for the fluid

$$\varepsilon\rho_f C_{Pf}\frac{\partial T_f}{\partial t} + \rho_f C_{Pf}\mathbf{u}\cdot\nabla T_f = \varepsilon k_s\nabla^2 T_s \,, \tag{12}$$

in which C is the specific heat of the solid, C_P is the specific heat at constant pressure of the fluid, k is the thermal conductivity.

Under the assumption of thermal equilibrium between the gas phase and the solid phase, one energy balance is sufficient to model the system. With

$$T_s = T_f = T \, , \tag{13}$$

adding Eq. (11) and Eq. (12)

$$(\rho C)_m \frac{\partial T}{\partial t} + (\rho C)_f (\mathbf{u} \cdot \nabla) T = k_m \nabla^2 T + q_s''' \, , \tag{14}$$

where

$$(\rho C)_m = (1-\varepsilon)(\rho C)_s + \varepsilon (\rho C_P)_f \, , \tag{15}$$

$$k_m = (1-\varepsilon)k_s + \varepsilon k_f \, , \tag{16}$$

respectively the overall heat capacity per unit volume and overall thermal conductivity.

The heat source in the solid bed is given by

$$q_s''' = \Delta H \, r_w \, , \tag{17}$$

where ΔH is the heat of reaction of the salt material and r_w is reaction rate of the water uptake. Since $(\rho C)_s >> (\rho C)_f$ from Eq. 15

$$(1-\varepsilon)(\rho C)_s \frac{\partial T}{\partial t} + (\rho C)_f (\mathbf{u} \cdot \nabla) T = k_m \nabla^2 T + q_s''' \, . \tag{18}$$

2.2 Constitutive equations

Heat capacity   The heat capacities as function of the temperature are taken from the work by Wendt et al. (1998).

Equilibrium pressure   According to the results provided by Kelley (1945) and Kipouros and Sadoway (1987), the equilibrium pressure of the salts are shown in Fig. 2
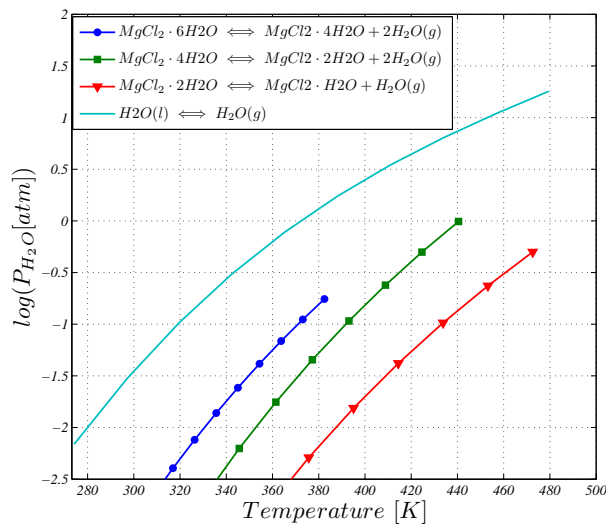

Figure 2: *Equilibrium pressures for solid salts and water vapor.*

Reaction kinetics   As suggested by Lebrun and Spinner (1989) the reaction for the dehydration rate can be expressed as

$$r_w = -C_a exp\left(-\frac{E_a}{RT_s}\right)\left(\frac{P_f - P_{eq}}{P_{eq}}\right) . \tag{19}$$

Since the values of the constants for the reactions have been not documented in the analyzed literature, an empirical approach is used, starting from the experimental results carried out on the lab-scale reactor at ECN. These constant values have been determined just for the dehydration process.

For the reaction

$$MgCl_2\cdot 6H_2O \longrightarrow MgCl_2\cdot 4H_2O + 2H_2O(g) ,$$

the following equation for the rate for the reaction it is used

$$r_{w1} = -19009200000 exp\left(-\frac{10038}{T_s}\right)\left(\frac{P_f - P_{eq}}{P_{eq}}\right) [kg_{water}/m^3\cdot s]. \tag{20}$$

For the reaction

$$MgCl_2\cdot 4H_2O \longrightarrow MgCl_2\cdot 2H_2O + 2H_2O(g) ,$$

it is used

$$r_{w2} = -22009200000 exp\left(-\frac{11428}{T_s}\right)\left(\frac{P_f - P_{eq}}{P_{eq}}\right) [kg_{water}/m^3\cdot s]. \tag{21}$$

In order to define when the shift from the first reaction to the second occurs, two conversion parameters are defined as as

$$X_{MgCl_2\cdot 4H_2O}(t) = \frac{\rho_{MgCl_2\cdot 6H_2O} - \rho_s(t)}{\rho_{MgCl_2\cdot 6H_2O} - \rho_{MgCl_2\cdot 4H_2O}} , \tag{22}$$

$$X_{MgCl_2\cdot 2H_2O}(t) = \frac{\rho_{MgCl_2\cdot 4H_2O} - \rho_s(t)}{\rho_{MgCl_2\cdot 4H_2O} - \rho_{MgCl_2\cdot 2H_2O}} . \tag{23}$$

The switch from the first reaction to the second, in the dehydration process, occurs when $X_{MgCl_2\cdot 4H_2O} \geq 0.98$ while the second reaction ends when $X_{MgCl_2\cdot 2H_2O} \geq 0.98$. The time for which $X_{MgCl_2\cdot 2H_2O} = 0.98$ is the overall reaction time is defined as τ.

Heat of reaction   Using the values for the heat of reaction and formation, provided by Kelley (1945) and converted in SI units, the heat of reaction as a function of temperature are calculated and reported in Tab. 1.

Table 1: *Heat of reaction in (kJ/kg_{H_2O}) as a function of the temperature in the form of $\Delta H = A + BT + CT^2$ with ($[T] = K$).*

Reaction	ΔH (kJ/kg_{H_2O})
$MgCl_2\cdot 6H_2O \rightleftharpoons MgCl_2\cdot 4H_2O + 2H_2O(g)$	$3229.7 + 0.1939T - 6.4548\cdot 10^{-4}T^2$
$MgCl_2\cdot 4H_2O \rightleftharpoons MgCl_2\cdot 2H_2O + 2H_2O(g)$	$3831.1 + 0.0348T - 6.4548\cdot 10^{-4}T^2$

3. RESULTS

The implementation of the system of equations has been done using the commercial software *COMSOL Multiphysics*. A validation has been made with the experimental results available and measured at *ECN* on the lab-scale reactor. In this work it will be carried out just the validation and simulation of the dehydration process. The cylindrical geometry, implemented in COMSOL, is 2D axial-symmetric and it is shown in Fig. 3. The reactor bed has a diameter of about 0.33 *m* and a height of 0.20 *m*. An external insulation layer of 3 *cm* thickness has been included. The simulation constants, for the lab-scale reactor, have been calculated and reported in Tab. 2.
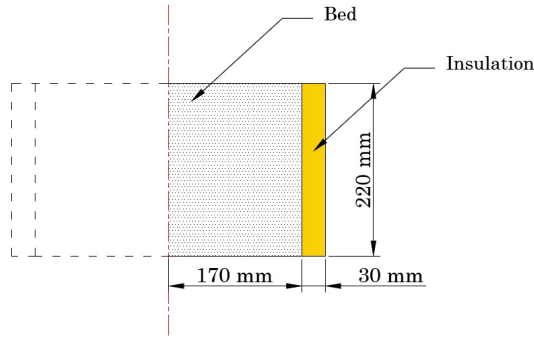
Figure 3: *2D axial-symmetric geometry of the lab-scale reactor.*

Constant	Value	Unit
u	0.1	m/s
$\rho_{MgCl_2 \cdot 6H_2O}$	1569	kg/m^3
$\rho_{MgCl_2 \cdot 4H_2O}$	1290	kg/m^3
$\rho_{MgCl_2 \cdot 2H_2O}$	1013	kg/m^3
K	$4 \dot{1}0^{-9}$	m^2
ε	0.7	–
k_s	0.704	$W/m \cdot K$
k_f	0.0328	$W/m \cdot K$
k_i	0.05	$W/m \cdot K$

Table 2: *Constants used in the simulation of the lab-scale reactor.*

However, several uncertainties about the measurements have led to difficult comparisons with the model simulation results. The two main uncertainness are:

1. The position of the thermo-couple in the bed. It is not clear the exact coordinate and moreover if they were bent during the experiments.

2. The air flow inlet has been considered constant and equally distributed in the model, while a small plate at the beginning of the inlet section may deviate the flux to the direction of the wall of the bed.

The temperature of the bed as a function of time has been compared with the experimental data of the lab-scale reactor. This comparison gives also an indication about the time in which the two dehydration reactions occur. In order to have a quantitative comparison between the experimental data and the model results, the root mean square error (RMSE) has been calculated as

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (x_i - \widehat{x}_i)^2}{n}} \qquad (24)$$

and reported in Fig. 4.

(a) Sensor at 2.7 cm
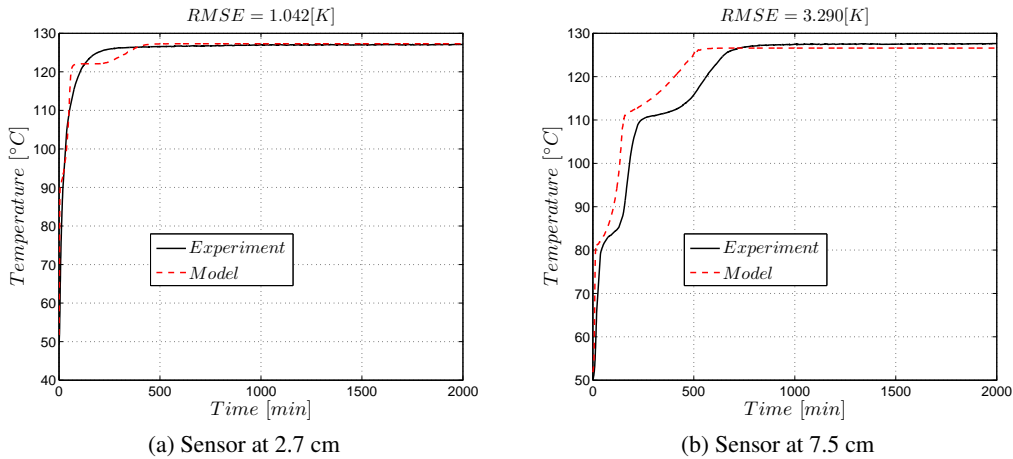
(b) Sensor at 7.5 cm

Figure 4: *Temperature in the bed from simulation results and experimental data at different bed location, during the dehydration process ($r = 14\,cm$).*

From Fig. 4 it is possible to notice that for the sensor located at 7.5cm the model predicts quite well (RMSE=3.290 K) the experimental results. There is a more significant deviation for the sensor at 2.7 cm: the 2 reactions in the experimental measurements are not visible. This might be explained considering that there is higher presence of an inert supporting material at the inlet of the bed and the reaction of the salt is really fast due to its low quantity in this region. Another explanation is that, for such a short thermo-couple ($2.7cm$), its thermal conductivity can induce to high errors in the measurements and, furthermore, it is not sure whether a micro channel of air surrounded the thermo-couple during the experiment.

In Fig. 5 is shown the temperature distribution inside the bed for different time steps.
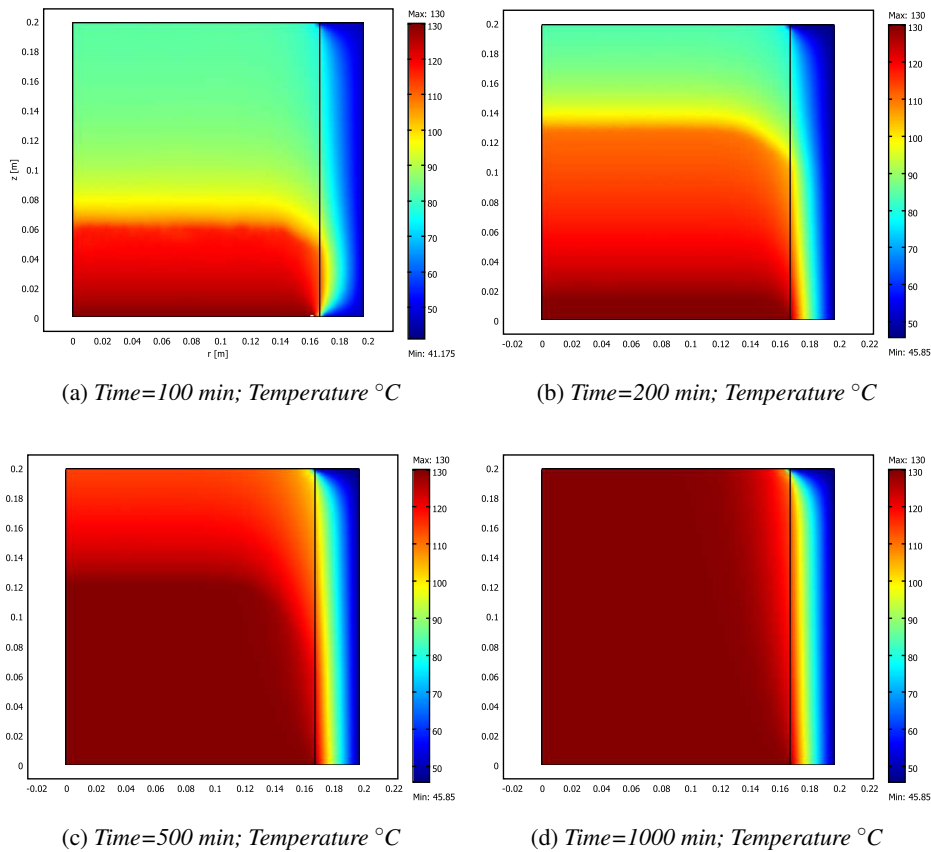
(a) *Time=100 min; Temperature °C*

(b) *Time=200 min; Temperature °C*

(c) *Time=500 min; Temperature °C*

(d) *Time=1000 min; Temperature °C*

Figure 5: *Temperature distribution in the bed for different time steps.*

4. CONCLUSIONS

A mathematical model for a thermo-chemical reactor for seasonal storage of solar heat is developed. The model for the 'open sorption' reactor calculates the advancement of the thermo-chemical reactions in time and spatial distribution. The model is validated using experimental results for the charging process of the heat storage. It predicts slightly faster dynamics compared to the experiments.

The model will be further refined and used to calculate the heat discharge process. It will furthermore be applied to study the effects of different reactor geometries and operating conditions on the thermal efficiency and on the overall energetic efficiency of the heat storage reactor. The results of that will provide indications for the reactor upscale.

ACKNOWLEDGEMENTS

NOMENCLATURE

C	specific heat (incompressible) ($J/kg \cdot K$)	C_P	specific heat at constant pressure ($J/kg \cdot K$)
C_a	pre-exponential constant ($kg/m^3 \cdot s$)	d	bed diameter (m)
c_F	dimensionless form-drag constant (-)	D_e	equivalent diameter of the bed (m)

d_p particle diameter (m)
E_a activation energy (J/mol)
h height of the bed (m)
ΔH heat of reaction (J/kg)
k thermal conductivity ($W/m \cdot K$)
K specific permeability (m^2)
$\mathbf{K}$ permeability tensor (m^2)
m mass (kg)
p partial pressure (Pa)
P total pressure (Pa)
q''' heat source rate per unit volume (W/m^3)
r radial coordinate (width) (m)
r_w water reaction rate ($kg/m^3 \cdot s$)
Re Reynolds' number (-)
t time (s)
T temperature (K)
u Darcy's velocity r-component (m/s)
$\mathbf{u}$ Darcy's velocity vector (m/s)
X conversion parameter (-)
w width of the bed (m)
z longitudinal coordinate (height) (m)

Greek symbols
ε void fraction of the bed (-)
ϕ_m mass flow rate (kg/s)
μ dynamic viscosity ($Pa \cdot s$)
ρ density (kg/m^3)
ξ mass fraction (-)
τ overall reaction time (s)

Subscripts - superscripts
da dried air
eq equilibrium
f fluid
i insulation
m mean
s solid
w water vapor
ws water saturated

Abbreviations
REV   representative elementary volume
RMSE   root mean square error
TCM   thermo-chemical material

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