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# Numerical Model of a $Ca(OH)_2$ / CaO thermochemical heat storage reactor


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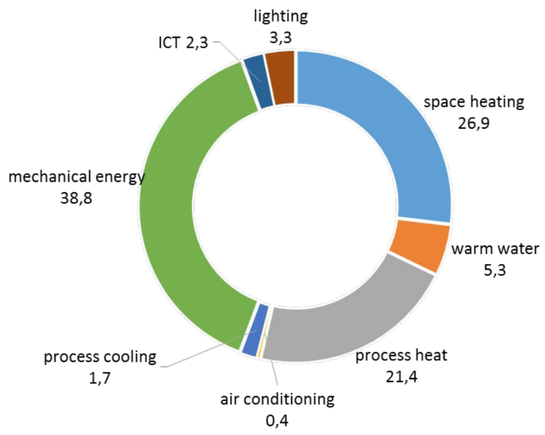
## Why store heat?

- Energy storage bridges the gap between fluctuating sources of renewable energy and energy consumption.
- Energy storage enhances energy efficiency and process optimization.
- Heat is the major part of the end energy consumption: 55,7 %
- decentralized technologies avoid transportation and conversion losses



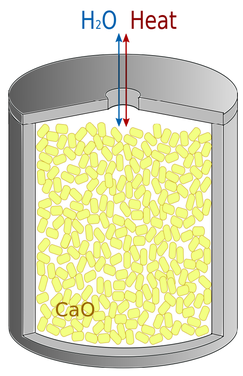

*end energy consumption in Germany in 2015; data of BMWi, see [2]*

## Storage concept

The heat is stored in the conversion of Calciumhydroxide $Ca(OH)_2$ to Calciumoxide CaO.

$$CaO_s + H_2O_g \rightleftharpoons Ca(OH)_{2,s} + \Delta H_R$$

with $\Delta H_R = 112\,\mathrm{kJ/mol}$




*schematic figure of a storage reacor*

*reactor concept testet at* DLR

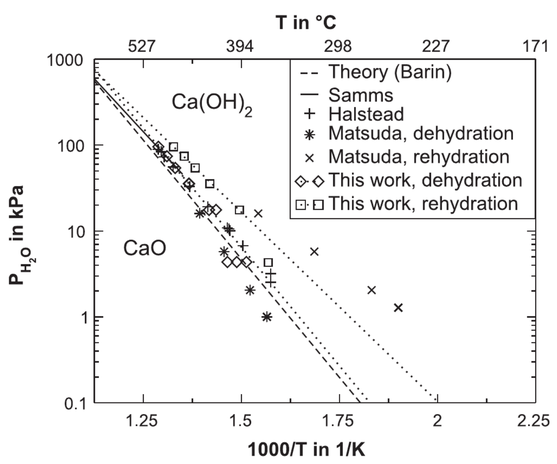
### Main Processes

- The reaction kinetics depends on the temperature and the partial water pressure. The equilibrium temperature is determined by the Van't Hoff equation [3].

$$T_{eq} = \frac{H^0}{R}\left(\frac{\Delta S^0}{R} + \ln\frac{p_v}{p_0}\right)^{-1}$$

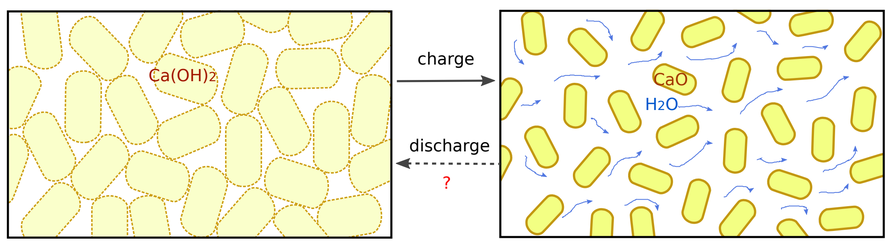
with $p_0 = 1.013 bar$

$T > T_{eq}$: charge
$T < T_{eq}$: discharge




*equilibrium temperature, see [4]*

- Volume change of about 50% of the solid particles during the reaction




### Advantages

- $Ca(OH)_2$ / CaO has high storage densities : 430 $kWh/m^3$
- $Ca(OH)_2$ / CaO is a cheap, abundant and environmentally friendly material
- $Ca(OH)_2$ / CaO can be operated as chemical heat pump

## Model concept

The numerical model is implemented in DuMu$^x$ [1] on the Darcy-scale.

It solves :

- mass and momentum balance equations for the gaseous phase consisting of the components air and water vapor
- mass balance equations for the solid phases CaO and $Ca(OH)_2$
- an overall energy balance assuming local thermodynamic equilibrium
- using linear reaction kinetics according to [5]

$$r_{hydration} = x_v(1 - x_{CaO,s})k_r^H\frac{T - T_{eq}}{T_{eq}}$$

$$r_{dehydration} = -(1 - x_{Ca(OH_2),s})k_r^D\frac{T - T_{eq}}{T_{eq}}$$

with $T_{eq}$: equilibrium temperature, $k_r$: reaction constants for hydration and dehydration

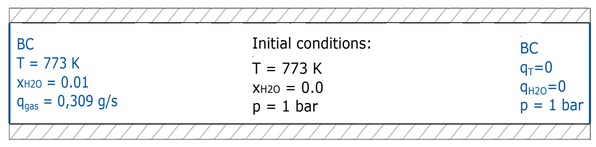
- accounting for the permeability and porosity change by the simplified Kozeny-Carman relationship as first approach :

$$k_{KC} = \left(\frac{1 - \Phi_0}{1 - \Phi_t}\right)^2\left(\frac{\Phi_t}{\Phi_0}\right)^3$$

with : $k_{KC}$: permeability factor, $\Phi_0$ : initial porosity, $\Phi_t$ : current porosity

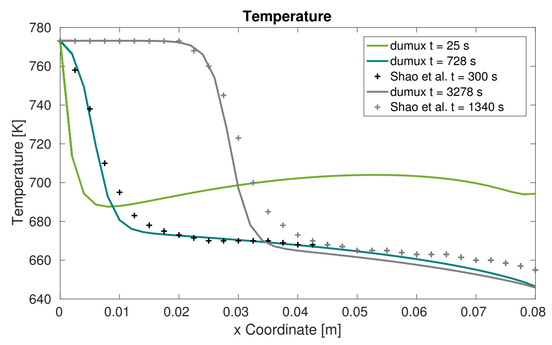
## Results and calibration

In order to test the numerical model, it was calibrated against the results of [5]. Initial and boundary were chosen accordingly:

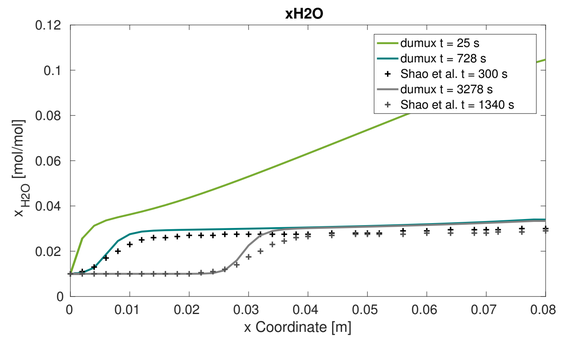



*Setup and boundary conditions*

The following figures compare the results of this study (dumux) with [5] (Shao et al.) at different times of one charging procedure.




temperature distribution vs reactor length




Water vapor distribution in the gas phase vs reactor length

## Challenges and Outlook

Due to the shrinking and swelling processes during the storage cycles the storage capacity changes over time. Cracks may be formed leading to preferential flow paths for the gaseous phase and less favorable conditions to the chemical reaction.

**Approach:**

- analyse the material behaviour of CaO/$Ca(OH)_2$ by using experimental data
- apply data integrated simulation science such as parameter estimation and data assimilation techniques to enhance the understanding of the system
- test different scenarios of the fracture development by numerical modelling

## Literature


[1] Ackermann, S., Beck, M., Becker, B., Class, H., Fetzer, T., Flemisch, B., Gläser, D., Grüninger, C., Heck, K., Helmig, R., Hommel, J., Kissinger, A., Koch, T., Schneider, M., Seitz, G., and Weishaupt, K. (2017). Dumux 2.11.0.

[2] BMWi, A. E. (2016). url: http://www.bmwi.de/de/themen/energie/energiedaten-und-analysen/energiedaten/energiegewinnung-energieverbrauch.html.

[3] Nagel, T., Shao, H., Singh, A., Watanabe, N., Roßkopf, C., Linder, M., Wörner, A., and Kolditz, O. (2013). Non-equilibrium thermochemical heat storage in porous media: Part 1–conceptual model. *Energy*, 60:254–270.

[4] Schaube, F., Koch, L., Wörner, A., and Müller-Steinhagen, H. (2012). A thermodynamic and kinetic study of the de-and rehydration of ca (oh) 2 at high h 2 o partial pressures for thermo-chemical heat storage. *Thermochimica acta*, 538:9–20.

[5] Shao, H., Nagel, T., Roßkopf, C., Linder, M., Wörner, A., and Kolditz, O. (2013). Non-equilibrium thermo-chemical heat storage in porous media: Part 2–a 1d computational model for a calcium hydroxide reaction system. *Energy*, 60:271–282.