



# Hydration and Dehydration of $\text{CaO}/\text{Ca}(\text{OH})_2$ for thermal energy storage – energy release and cyclability

Holger Urs Rammelberg<sup>1\*</sup>, Thomas Schmidt<sup>1</sup>, Wolfgang Ruck<sup>1</sup>

<sup>1</sup>University of Lüneburg, Institute for Ecology and Environmental Chemistry, Scharnhorststr. 1/13, 21335 Lüneburg – Germany  
\*Rammelberg@leuphana.de, 49-4131-6771768

## Introduction

The change from fossil energy resources to renewable energy resources needs higher efficiency in energy conversion and utilization. Concentrated solar power (CSP), enables the utilization of electricity and heat, using solar radiation as input. Here thermal energy storage is a key component. [1] Thermal energy storage is needed also for high efficiency compressed air energy storage (CAES) to store electricity energy without loss of heat in process. In comparison to most commonly used water or molten salt storage, thermochemical storage materials provide ten times or even higher storage capacities per mass or volume and the ability to store heat for longer times without the need of insulation [2]. Recently published results state  $\text{Ca}(\text{OH})_2$  to be useful for higher temperature levels [3].

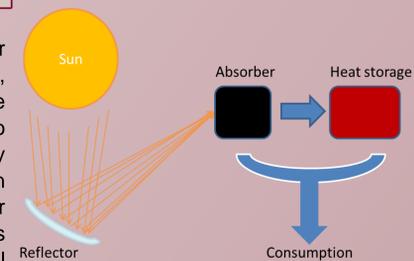


Figure 2: CSP principle with heat storage



Figure 1: Concentrated solar power plant

## Materials and methods

The reaction we investigated is the following reversible reaction:  $\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + \text{heat}$ . We used a simultaneous TGA/DSC System to analyze heat fluxes and changes in sample mass during hydration and dehydration experiments (Figure 3). Dried nitrogen has been used as purge gas at a flow rate of 50 mL/min. For dehydration, we additionally used a humidified separate nitrogen flow. The humidity of the mixture gas was measured at the oven outlet and used for calculation of the water vapour partial pressure inside the TGA/DSC oven. Further details can be found in [4].

Investigations on the cycling stability of the  $\text{Ca}(\text{OH})_2$  were done by multiple measurements of the integrated hydration heat fluxes of one sample during consecutive dehydration/hydration cycles. The temperature program used for dehydration of the samples prior to the hydration was set to ramp up from 35 °C to 600 °C at 5 °C/min, and then to cool down at -5 °C/min to 35 °C. The hydration process was conducted at different temperatures between 35 °C and 450 °C and the moist nitrogen gas was switched on after a settling time of 5 min to start the hydration of the sample. The moist nitrogen gas flow was varied from 25–150 mL/min, corresponding at 35 °C to a water vapor pressure in the oven ranging from 12-21 hPa during hydration.

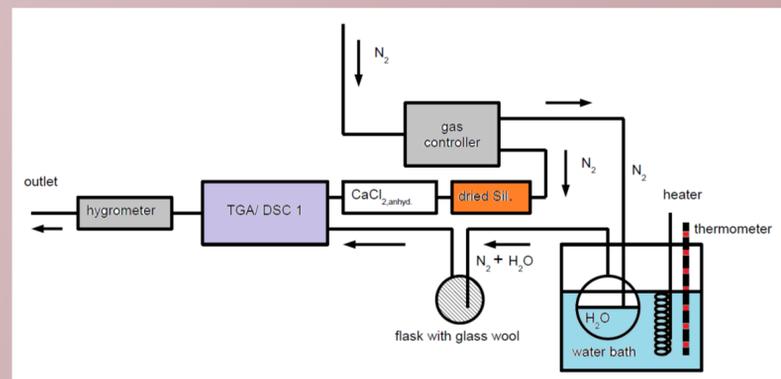


Figure 3: Experimental setup

## Results and discussion

### Cycle measurements

During the full hydration and dehydration, the hydration enthalpies of  $\text{CaO}$  and the dehydration enthalpies of  $\text{Ca}(\text{OH})_2$  were measured over 22 cycles, respectively. Apart from a few outliers,  $\text{CaO}/\text{Ca}(\text{OH})_2$  showed an increase in heat storage capacity and weight with an increasing number of cycles (figure 4). The slope of both parameters was very similar. The condensation enthalpy was calculated with the weight difference between two cycles and was compared with measured enthalpy. We were able to count out the condensation enthalpy as the sole factor of the enthalpy increase. The calculated condensation enthalpy equals 46 % of the total enthalpy after 22 cycles. This value is in good agreement with calculations based on literature enthalpy data (42 %). [5] Furthermore, we noticed a decongestion of  $\text{CaO}/\text{Ca}(\text{OH})_2$  when cycling, together with an increasing volume, leading to a more porous structure.

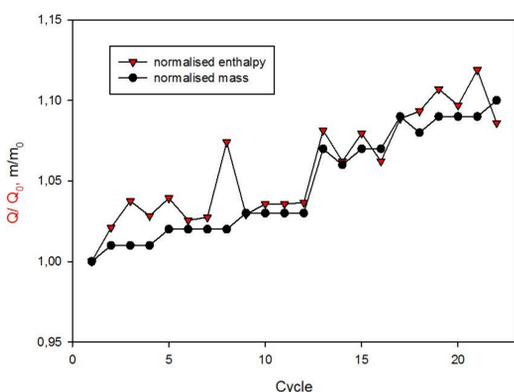


Figure 4: Cycle measurements

### Completeness measurements

We also studied the hydration of  $\text{CaO}$  at different temperatures between 35 °C and 450 °C and at water vapour flow rates between 25 mL/min and 150 mL/min. Figure 5 shows that the normalized completeness of hydration (CH) is located in the field of 0.9 to 1.0 in a temperature range of 35 °C to 250 °C. Above 100 °C the CH fluctuates much more, with two outliers at 150 °C and 200 °C. Above a temperature of 250 °C no hydration was measured and evaluated with exception of one hydration at 350 °C and water vapour flow rates of 150 mL/min with CH of 0.80 (undrawn).

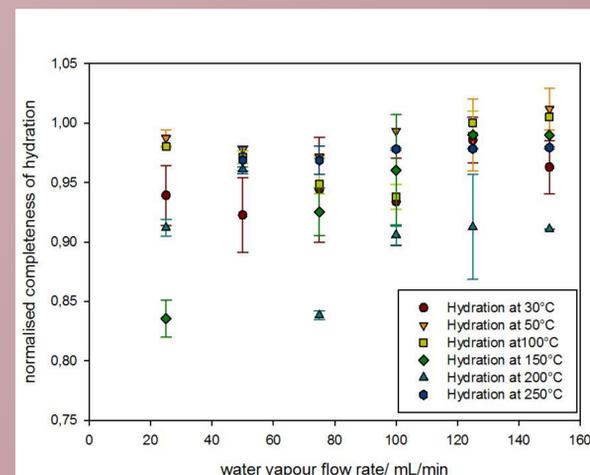


Figure 5: Completeness hydrations (CH) measurements

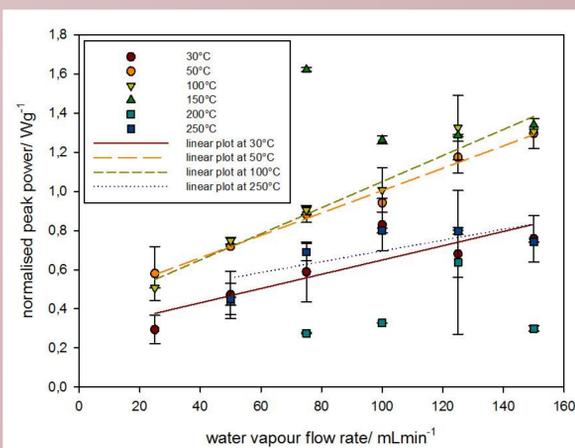


Figure 6: Peak Power

### Peak power

Figure 6 shows the normalized peak power versus to the water vapor flow rate. In the temperature range between 35 °C and 100 °C, a linear response of peak power and water vapour flow rates can be identified. Above 100 °C the peak power shows no such correlation. At 150 °C there appears no correlation with the water vapour flow rate and the highest peak power was given. The experiments conducted at the water vapour flow rates of 125 mL/min and 150 mL/min showed the highest peak power. Measurements above temperatures of 150 °C showed lower peak power.

## Conclusions

- The  $\text{CaO}/\text{Ca}(\text{OH})_2$  thermochemical storage system shows good cycle stability, which is needed for high temperature applications.
- The hydration was completed in a wide temperature range between 35 °C and 250 °C and offered the highest normalised peak power at temperatures in range of 150 °C.
- Above 250 °C, the hydration seemed to be largely inhibited, which leads to an unsatisfying discharging characteristics.

## Literature

- [1] Gil, A., Medrano, M., Martorell, I., Lázaro, A., Dolado, P., Zalba, B., Cabeza, L. F., State Of The Art On High Temperature Thermal Energy Storage For Power Generation. Part 1-concepts, Materials And Modellization, Renewable And Sustainable Energy Reviews 14, 31-35, 2010.
- [2] Fisch, N., Bodmann, M., Köhl, L., Saße, C., Schnürer, H., Wärmespeicher. Bine Informationsdienst, 4th Edition, Bonn 2005.
- [3] Schaub, F., Wörner, A., Müller-steinhausen, H., High Temperature Heat Storage Using Gas-solid Reactions. Conference Proceedings Of The Effstock 11th International Conference On Energy Storage, June 14-17, Stockholm, Schweden, 2009.
- [4] Opel, O., Rammelberg, H.U., Gérard, M., Ruck, W., Thermochemical Storage Materials Research - TGA/DSC-Hydration Studies, prepared for International Conference on Sustainable Energy Storage 2011, February 21.-24., Belfast, Ireland 2011.
- [5] Ogura H, Ishida H, Kage H and Mujumdar A S, 2003 Enhancement of energy efficiency of a chemical heat pump - assisted convective dryer, Drying Technology, 21, 279 – 292