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Résumé en français.

Les matériaux de stockage d'énergie thermo-chimique ont un intérêt certain du fait de leur capacité de stockage élevée. L'ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) présente en plus l'avantage d'une température de stockage adaptée autour de $60\text{ }^\circ\text{C}$ et un prix abordable qui pourrait convenir au stockage d'énergies renouvelables pour le chauffage des bâtiments ou la production d'eau chaude sanitaire. Le ciment sulfo-alumineux (CSA) est utilisé comme le moyen de stockage d'énergie thermo-chimique. Un prototype a été construit pour évaluer les propriétés de stockage d'un monolithe constitué d'une pâte de CSA. Un débit d'azote à haute température peut être produit pour déshydrater le CSA et stocker de l'énergie. En mélangeant l'azote à de la vapeur d'eau, l'énergie pouvait alors être restituée à la demande. Pour faciliter la diffusion du gaz, la pâte de ciment était moussée pour augmenter la perméabilité. Environ 43 MJ/m^3 (12 kWh/m^3) d'énergie pouvait ainsi être restituée en deux jours lorsque le matériau était hydraté.

Thermochemical energy storage in a CSA-based cementitious material

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Abstract

Thermochemical energy storage materials are found promising due to their high capacity of storage. Ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) presents additional benefits of a moderate temperature of storage (60°C) and an affordable price that may fit the prerequisites to store renewable energies for space heating or domestic hot water production. CSA (Calcium Sulfo-Aluminate) cement was used as a thermochemical energy storage media. A prototype was built to evaluate the storage properties of a monolith made of CSA cement paste. A hot dinitrogen flow would be produced, to dehydrate CSA cement and store energy. By adding water vapor to the nitrogen, the energy could then be released on demand. To facilitate the diffusion of the gas flow, the cement monolith was foamed, increasing its permeability. It was shown that about 43 MJ/m^3 (12 kWh/m^3) could be released within two days when the material was hydrated.

Keywords: Thermochemical energy storage; ettringite cementitious material; hydration-dehydration;

Introduction

The possibility of energy release by ettringite was demonstrated by Struble and Brown [1], who found a heat of hydration close to $1,4 \text{ MJ/kg}$. The process involved is the dehydration of ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) into meta-ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 12\text{H}_2\text{O}$), resulting in the physical and chemical desorption of water. Dehydration of the material goes by step, as demonstrated by Zhou and Glasser [2]. It was found that dehydration was complete (20 molecules evaporated) as a temperature of 57°C was experienced by the material in a dry atmosphere (partial pressure of vapor of 800 Pa).

The high heat of reaction and adequate temperature for energy storage resulted in the development of several prototypes. These prototypes involve either closed (Figure 1 (a)) or open systems (Figure 1 (b)). At EMPA was developed a closed system prototype involving a 6 m^3 cement block, releasing 216 MJ/m^3 on discharge [3]. Two other prototypes of 0.005 m^3 were developed at LMDC. The first was a closed-system, showing 220 MJ/m^3 on discharge, while the second was an open-system prototype for better efficiency on release (421 MJ/m^3), that was foamed material (76% porosity) [4]. No aging was found for these samples after 10 cycles. To allow the gas to go through the material, the material was foamed, resulting in a porosity of 53%,

and a density of 600 kg/m^3 instead of 1800 kg/m^3 for the bulk material.

This paper presents the study of a new prototype, developed to characterize open-system at a larger scale.

Materials and method

Production of the cementitious monolith

The material considered is ettringite, based on CSA cement (Vicat, Alpenat R²). The material was mixed with water, and a foaming agent (hydrogen peroxide, J.T. Baker®). A monolith of 0.047 m^3 was obtained, which was assumed to contain about 68% of ettringite [5]. A resin was applied on the edges for sealing and forcing the heat transport fluid to cross the material. Due to scale-up from 0.005 m^3 samples, the porosity was decreased to 53%, for a density of 0.869 and a compressive strength of about 3.5 MPa to avoid coalescence.

Development of a prototype

A fully new prototype was used for this characterization, presented in Figure 2. The cementitious monolith was placed in the reactor, and different elements were placed before for heat transfer gas conditioning. A dinitrogen flow was considered instead of air to avoid carbonation of ettringite which would lead to a decrease of the storage capacity of the material. Once produced, a 3-way valve was used to conduct the gas either throughout “heater” or

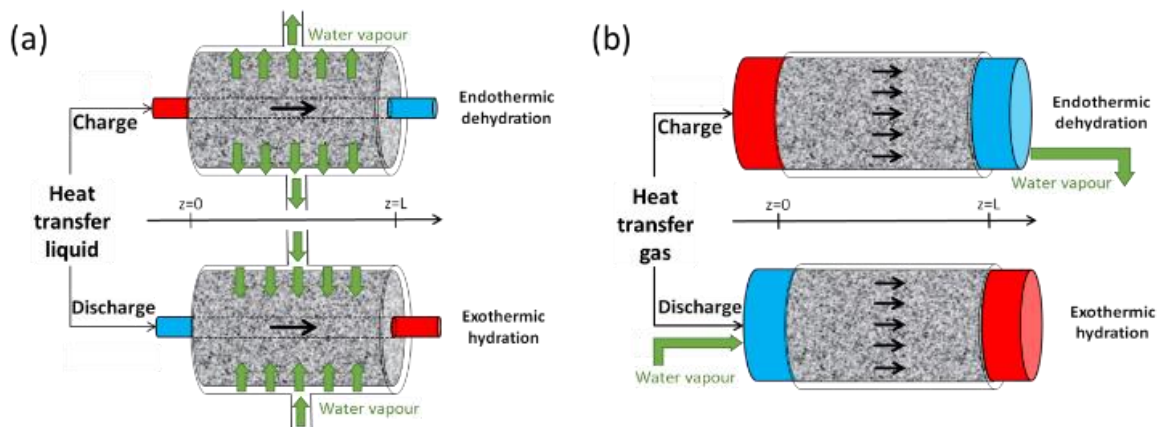


Figure 2. (a) closed configuration and (b) open configuration.

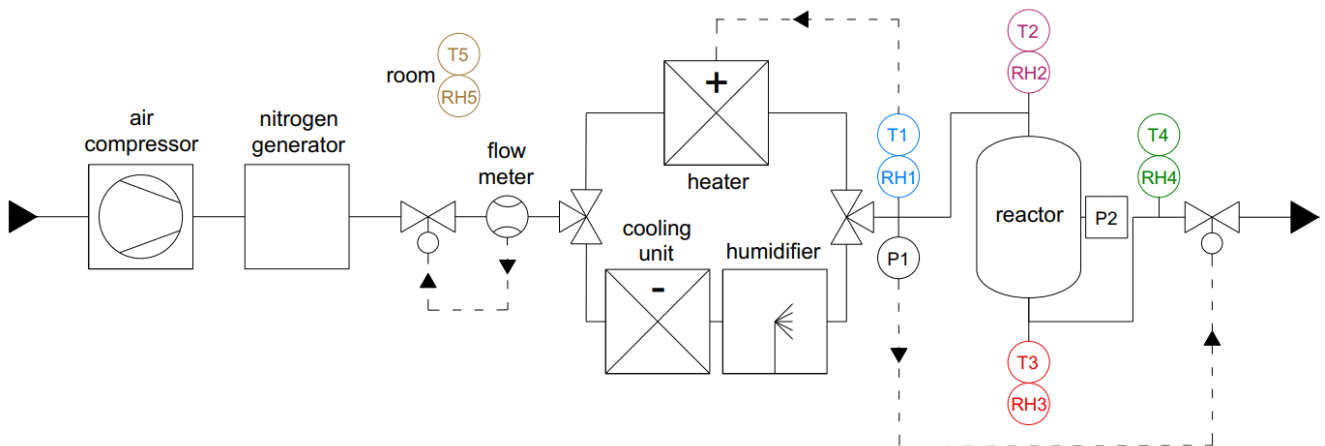


Figure 1. Schematic description of the different functions of the prototype. The dashed path with arrows corresponds to the retroaction of the measurement on flow, pressure, or heating, of nitrogen. The colors of the sensors correspond to their curves in the following figures.

“cooler+humidifier” unit. On one side, the heater was used to increase the temperature of the gas, which would dehydrate the reactive material. On the other side, the humidifier allows for water vapor mixing with the heat transport fluid. Along the path, several sensors were positioned for measuring and controlling by PID the parameter of the heat transport fluid. A flowmeter (Azbil, MCF0150) and a manometer, named P1 on Figure 2 (S+S Regeltechnik, SHD-SD I-10), each connected to a hydraulic valve to control flow and pressure. To evaluate the quantity of energy stored, five temperature/relative humidity (RH) sensors (Galltec Mela, SZKA.0H model) were positioned before and after the reactor, as seen in Figure 3.

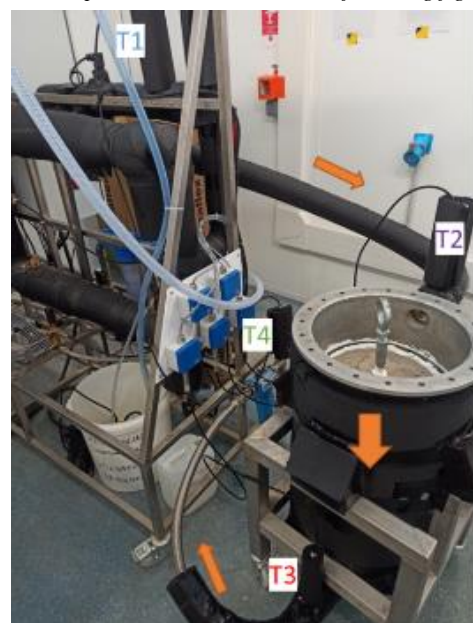


Figure 3. Photo with the distribution of the Pt100/humidity sensors (T1, T2, T3, and T4). The arrows represent the direction of the gas flow. The font colors correspond to the color of the curves in the following figures

Results and Discussions

Temperature and relative humidity calibration

Before the experiments, the calibration of the temperature and humidity sensors was performed. For the calibration in temperature, the probes were immersed in a thermostatic bath filled with water. A nitrile glove was used to avoid penetration of liquid water in the probe, as shown in Figure 4 (a). The probes were tested with 4 temperatures of 30; 45; 60 and 75 °C and left immersed for ten minutes for each temperature. In parallel, the calibration in relative humidity was carried out by immersing the probes in an insulated volume containing air saturated by solutions of salts (Figure 4 (b)). The 3 solutions of salt considered were NaOH, MgCl₂ and NaCl, producing a relative humidity of 9; 33 and 75%.



Figure 4. Calibration in (a) temperature and (b) humidity of the sensors

For temperatures, a standard deviation of ± 0.15 K from the set point was found, and for humidity, the deviation was about 0.5%RH, these data were consistent with the datasheet.

Charge curve

The experiment of thermochemical charge and discharge was then carried out by respectively heating and hydrating a cementitious monolith. This experiment was performed by fixing a nitrogen flow of 0.5 bars and 12 Nm³/h (flow rate given for standard conditions). The evolution of the temperatures for the heating curve is presented in Figure 5. A temperature of 60 °C is immediately reached before the material, while a temperature of 50 °C was found after the material, due to the thermal inertia of cement. After stabilization, the remained temperature gap between inlet (T2 = 63 °C) and outlet (T3 = 52 °C) may be explained by heat loss.

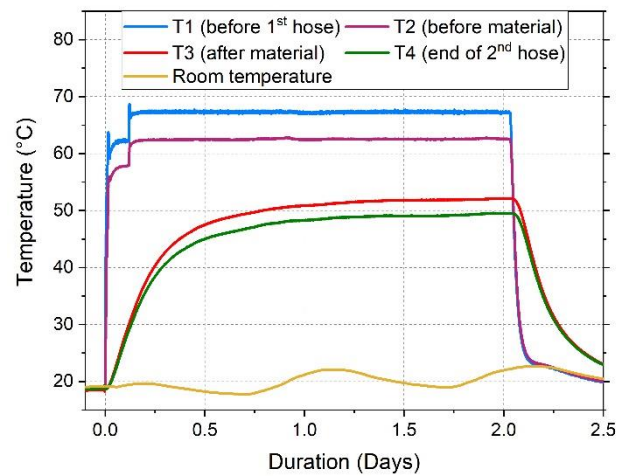


Figure 5. The temperature evolution during heating (storage) of the cementitious material. The position of the probe can be seen in Figure 3 and Figure 4

Cooling to ambient temperature

After two days at a setpoint of 70 °C, the sensible heat stored is released by stopping the heater. In order to determine the quantity of heat released, heat capacity measurements were performed using DSC (Netzsch, STA 449 F3 Jupiter). It was found a heat capacity of about 850 J/kg/K. With a weight of 36 kg, the cooling of the monolith to ambient temperature released about 2.2 MJ/m³ (0.61 kWh/m³) considering a decrease in temperature from 55 to 20 °C.

Discharge curve

The release of heat is initiated by adding water vapour to the heat transport fluid. In Figure 6 is presented the evolution of the temperature difference between the inlet and the outlet of the reactor, during the heat release step. A difference of +7 °C is found a few hours after the release of energy. The heat extraction is facilitated by forced convection using a heat transport gas passing through the material. After one day, a stabilization of this difference is found around 1 °C.

By integrating the energy released from the monolith (36 kg; 0.047 m³) over time, about 1.83 MJ (0.51 kWh) can be released by physical and chemical sorption from the material. This corresponds to 43 MJ/m³ (12 kWh/m³), a thermochemical energy storage of about 20 times more than the sensible energy storage capacity.

To reach the theoretical value of energy release, several technological improvements of the prototype and the material are expected. This could involve an increase in the permeability of the material, relative humidity in the heat transport gas during discharge, or thermal insulation.

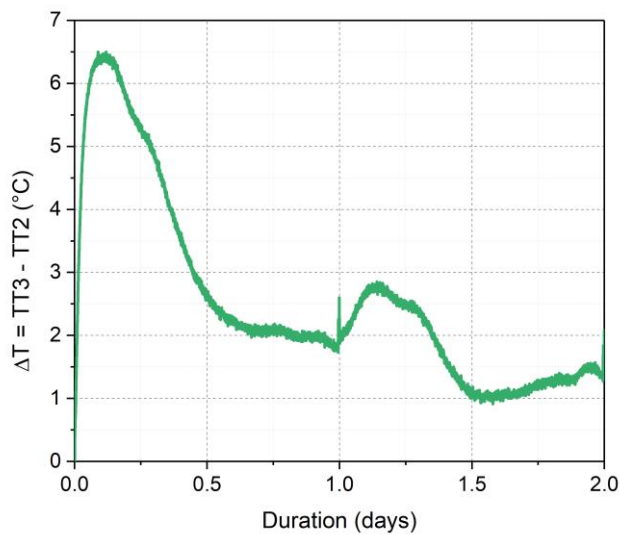


Figure 6. Evolution of the temperature difference
 $\Delta T = TT3$ (reactor outlet) - $TT2$ (reactor inlet)

Conclusions

This repeatable reaction of hydration from meta ettringite to ettringite shows promising results for thermochemical energy storage at large scale, at a temperature adapted to residential and industrial applications. The capability of energy release from a large-scale material has been demonstrated for an innovative prototype. This prototype involves the use of heat transport fluid for the mass transfer of water vapor, also called an open system, resulting in a release of 43 MJ/m³.

The cementitious material is also cheap, easy to produce, and presents a mechanical resistance of 3.5 MPa. In addition to a self-supporting material, its applications scope is larger as the material can be used as large-scale storage tank. Able to store energy without heat loss when it is insulated from water vapor, this material can be easily used for thermal energy transport to another location.

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