

Experimental Investigation of hot Water Generation from Small CaO/Ca(OH)₂ Thermochemical Energy Storage System

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Abstract. Thermochemical energy storage (TCS) is a very promising method for energy applications, storage, transport and thermal generation because of its high energy density and negligible heat loss. Several storage materials are being explored, in which CaO/Ca(OH)₂ is among the most attractive systems for further investigations. In this work, a small Ca based TCS system was developed, built and tested for hot water generation. Hydration and dehydration reactions involving CaO and Ca(OH)₂ powders were performed. Performance in terms of temperature rise in heat transfer fluid and its efficiency during successive discharging/charging cycles was evaluated and discussed.

1. Introduction

Energy storage is crucial in balancing supply and demand of energy. It enables increasing utilization and contribution of renewable energy, helps reduce energy consumption and minimise environmental pollution [1]. One of the established energy storage technologies is thermal energy storage. It is defined as temporary storage of thermal energy in the form of hot or cold substances for later use. There are three main types of thermal energy storage, namely sensible, latent and thermochemical [2]. Thermochemical energy storage (TCS) is considered to be highly attractive as it can provide higher energy storage density than the other types [3]. TCS is mainly based on a reversible chemical reaction: $C + \text{Heat} \leftrightarrow A + B$. When material (C) absorbs external heat (solar, geothermal or industrial waste heat) and decomposed into A and B. The materials (A and B) are divided by physical means and stored in different containers. When materials A and B are combined together, the reverse reaction occurs generating C and releases the stored chemical energy. As long as the energy storage system is constituted by a closed loop and appropriately stored, the energy storage period is theoretically unlimited. Generally, a TCS system can be divided into three main processes: charging, storing, discharging [4], shown in Figure 1.

TCS material is a critical component of the storage system. The performance depends on the operating conditions, cycle stability, and operating cost. An appropriate storage medium is extremely important when establishing a storage system. Desirable properties for good thermochemical materials include (i) high energy density; (ii) good heat-transfer performance; (iii) being environment friendly and reasonable cost; (iv) no side reaction under the operating conditions; and (v) excellent cycling stability and high conversion rate. So far, more than 70 kinds of thermochemical reaction have been studied [1-5]. A Ca based CaO/Ca(OH)₂ hydration/dehydration reaction couple appear to be among the most suitable TCS system [6].



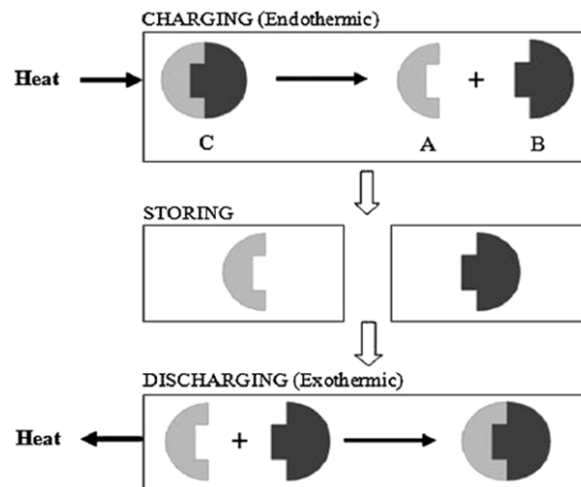


Figure 1. Processes in closed TCS cycle: charging, storing and discharging [4].

At present, the $\text{CaO}/\text{Ca}(\text{OH})_2$ system has been intensively studied by a number of researchers. Equation (1) shows the basic reaction principle of inorganic hydroxide system. Energy changes during $\text{Ca}(\text{OH})_2$ dehydration and rehydration process are shown in Figure 2. It can be seen from that at atmospheric pressure, an input energy 148.6 kJ is needed for decomposing 1 mol $\text{Ca}(\text{OH})_2$ at 25 °C into CaO and H_2O at 510 °C. If CaO is stored as a solid at 25 °C, and the product water is condensed into liquid water at 25 °C then, 85 kJ heat is released as a form of sensible and latent heat. Thus, the remaining 63.6 kJ is actually stored in the form of chemical energy, which is equivalent to 43% of the total input energy.

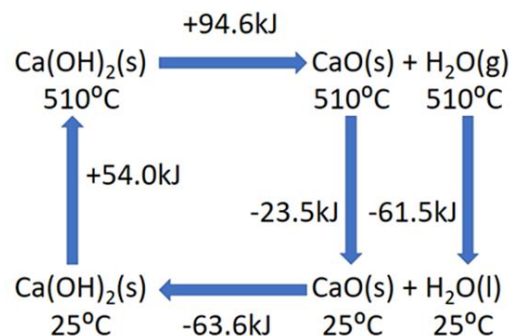


Figure 2. Energy storage/release process in a $\text{Ca}(\text{OH})_2/\text{CaO}$ system.

$\text{Ca}(\text{OH})_2$ dehydrates between 400 and 508 °C with the water vapor partial pressure ranging from 0.1 to 1 bar, so it can be used to store high-temperature thermal energy. CaO can be stored at room temperature for a long time. When water vapor is passed into reactors filled with CaO , the reverse exothermic reaction occurs and generates high-grade heat. The $\text{CaO}/\text{Ca}(\text{OH})_2$ system has many advantages, such as high storage density, fast reaction kinetics, stability and safety, being nontoxic and having low price, and thus has attracted enormous attention especially in concentrated solar power and combine heat and power.

For the $\text{CaO}/\text{Ca}(\text{OH})_2$ system, one of the dominant disadvantages is related to poor mechanical performance of the material. CaO particles are known to break during hydration/dehydration reactions which can become entrained by the gas and create large pressure drop. A direct-type reactor proposed by Schaube et al. [7] utilized powder reactants was found to perform well but with losses from

pressure drop. Research on TCS reactor systems remain to be explored. Further research is still needed to gain better understanding in designing these systems, to improve their efficiencies, and to address other practical issues. In this work, a small TCS unit based on the $\text{CaO}/\text{Ca}(\text{OH})_2$ system was developed. The powder reactants were used. Its performance was investigated.

2. Materials and Methods

2.1. Material

For the initial reactant, CaO was purchased and obtained from Elago Enterprises Pty Ltd., based on the products data sheet showed in Table 1.

Table 1. Specification of calcium oxide.

	Specification
Assay	90.0% minimum
Description	White powder
Identity (FTIR)	conforms
Insoluble matter in HCl	0.5% maximum
Chloride (Cl)	0.05% maximum
Sulphate (SO_4)	0.5% maximum
Heavy metals (as Pb)	0.005% maximum

2.2. Experimental setup and procedure

Figures 3 and 4 show schematics of the experimental setup and actual reactor and heat exchanger used in the experiment. For each experiment, a total of 28 g CaO or $\frac{1}{2}$ mole was used. It was initially loaded into the cylindrical container acting as the reactor.

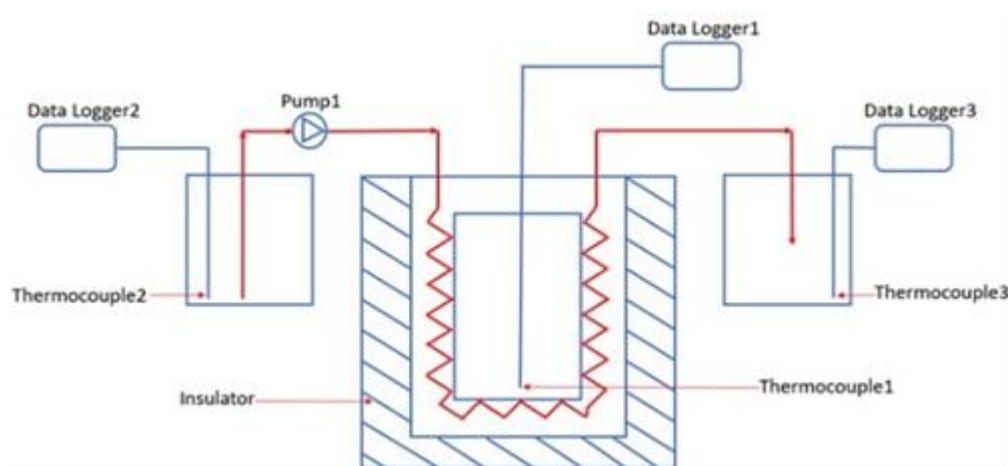


Figure 3. Layout of the reactor and experimental setup.

For discharging process, the initial temperature of the fresh sample of CaO and the reactor was recorded. The water syringe was started to deliver jet spray of liquid water of 9 g into the reactor for hydration reaction. The hydration reaction was started. The temperature in the reactor was increased. Water was used as a heat transfer fluid in with flowrate of 0.1 Lpm. Once the reactor reached the maximum temperature, the pump was kept switched on for circulating the cooling water to receive the energy release from the chemical energy until there was no temperature difference between the reactor

and heat transfer fluid. The data recording process was started immediately after delivering the sprayed water and monitored continually over the reaction (heating) and cooling period for a further 30 min. Since the specimen was a homogeneous and isotropic material, and housed in an insulated chamber, heat generation was expected to be uniform with the exothermic reaction. The transient temperature response was measured and recorded at the center of the material. The reaction time for each cycle was about 20 min. For charging process, in order to reuse the hydrated specimen, it was dehydrated in a furnace at 600 °C for about 60 min and was allowed to completely cool down overnight before being used again.



Figure 4. Reactor and heat exchanger arrangement.

2.3. Energy analysis

The net input energy is equal to the energy released by the reaction (enthalpy of formation). An energy balance for this process is as follows [8]

$$-(\text{Energy recovered} + \text{Heat loss}) = \text{Energy accumulation} \quad (2)$$

where the energy accumulation is a negative value equivalent to the energy released during the exothermic reaction. Energy efficiency of this process is evaluated from the energy recovered by the working fluid divided by the heat of reaction as follows:

$$\eta = \frac{m_d C_{pw} (T_2 - T_1)}{\Delta H_R} \quad (3)$$

3. Results and Discussion

During hydration of CaO, rapid rise in temperature at the beginning was observed. Once maximum temperature of the reactor was reached, heat transfer water was operated in which cooling was enabled. Temperature rises from room condition were in the range of 45 – 50°C. Table 2 is the summary of the maximum temperature recorded for the discharging in the reactor ranging between 72 and 82°C (an average maximum temperature of 76.1°C). Figure 5 shows the sequence of repeated cycles 1, 2, 3 and 4 for the reactor temperature and water outlet from heat exchanger of fresh/dehydrated samples of CaO. The energy efficiencies were found to be in the range of 60 – 83%.

Table 2. Summary of maximum recorded temperatures (reaction of ½ mole CaO and ½ mole H₂O)

	Storage material		Mass of H ₂ O	Maximum reactor temperature (°C)	Maximum water outlet of heat exchanger (°C)
	Condition	Initial temperature (°C)			
1	Fresh CaO	30	9.0	72	43
2	Dehy. CaO	30	9.0	82	44
3	Dehy. CaO	25	9.0	73	41
4	Dehy. CaO	27	9.0	77	41

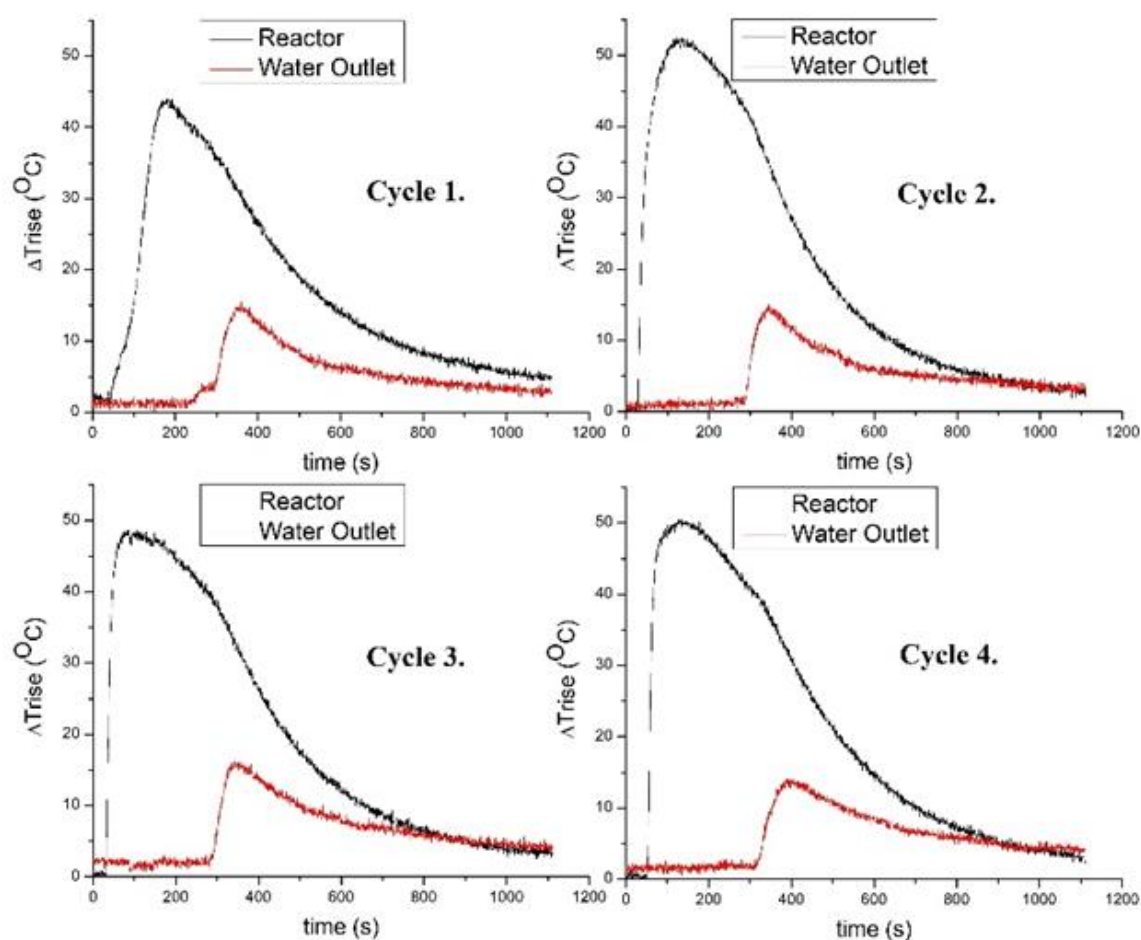


Figure 5. Discharging sequence of cycles 1,2,3,4.



Figure 6. Agglomeration of powders in the reactor after hydration reaction.

It was also observed that agglomeration of powders formed inside the bed, as shown in Figure 6. This might result in local non-uniformity in flow distribution that would affect the reaction. It was suggested that addition of nanoparticles may ease this problem [9].

4. Concluding remark

A small TCS unit based on the $\text{CaO}/\text{Ca}(\text{OH})_2$ system has been built to generate hot water in this work. Its performance in terms of hot water generation, thermal efficiency and cyclic behaviour was

investigated. Hydration reaction rates was immediate with rapid temperature rise. High thermal efficiencies were realized. Nonetheless, greater effort must be exerted to test the reactor setup continuously and to enhance the heat output.

5. Reference

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