Thermochemical energy storage using calcium oxide

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Abstract The possibility of using the thermochemical energy storage system $CaO/Ca(OH)_2$ for domestic applications has been studied. The suggested concept is based on the use of solar tower power plants for the dehydration of calciumhydroxide $Ca(OH)_2$. The produced calciumoxide CaO can be delivered to the consumers where it can be hydrated using water in the liquid state. The produced thermal energy can be utilized in room and water heating. 10 experiments were performed on the hydration-dehydration cycle of the system $CaO/Ca(OH)_2$. A solar concentrator with fixed focus was used in the dehydration steps. It is found that the whole hydroxid material could be dehydrated in all experiments without any degradation. The resulted temperatures during the hydration process could be controlled by variation of the ratio between water and calcium oxide.

**Keywords** Thermochemical solar energy storage; $CaO/Ca(OH)_2$ cycle

1. Introduction

In 2015, 195 countries ratified the Paris Treaty on Environmental Protection, which set a goal of reducing greenhouse gas emissions to zero by 2050 (United nations, 2015). Achieving this goal will require large-scale investment in renewable energies and a reduction in fossil fuels consumption as much as possible. However, the intermittent nature of renewable energies makes any successful investment of these energies dependent on the possibility of storing part of it for use in the times when it is absent.

Thermal storage of solar energy is an essential technology to benefit from this energy in times of absence of the sun or at times when the intensity of solar radiation is not sufficient to secure the demand for energy. Solar thermal storage technologies are inexpensive, environmentally friendly, and based on widely available materials.

Thermochemical storage technology is considered a promising technology because of its advantages compared to other technologies, as the energy storage density is much higher and losses during the storage phase are zero; additionally, the temperature at which the stored energy is released can be adjusted within a relatively wide range (Schmidt, 2017). The $CaO/Ca(OH)_2$ storage system has received a lot of attention and research has been conducted with a view to its use in thermal energy storage in Concentrated Solar Power Plants (CSP). This system is based on the reversible reaction:

$$CaO + H_2O \leftrightharpoons Ca(OH)_2 + 104 \ (kJ/mol) \qquad (1)$$
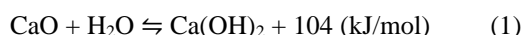
The previous reaction has different advantages such as high enthalpy, calcium oxide is abundant and cheap, and the stored energy can be released at high temperatures (600 °C or more) allowing for thermodynamic cycles with high carnot efficiencies (Schmidt, 2017).

In the first stage of the storage process, calcium hydroxide is dried at high temperatures in an energy-absorbent reaction, dissolving into calcium oxide and water vapor. This process is called "charging". The reverse reaction between water and calcium oxide releases energy and is called "discharging". The water in the discharge process

can be liquid or steam, according to the required temperatures. If steam is used, higher temperatures can be obtained.

Most of the internationally published research regarding the use of the system $CaO/Ca(OH)_2$ in energy storage focused on the benefits of this system in concentrated solar solar power plants (CSP). As for the domestic uses of space and water heating, there are no adequate studies (Pardo et al., 2014; Schaube et al., 2011; Brown et al., 1992).

The stability of the reaction after a large number of charge and discharge cycles is important and a fundamental factor in choosing an energy storage system. Schaube demonstrated in a set of laboratory experiments the stability of the reaction (1) after 100 charge and discharge cycles (Schaube et al., 2012), Therefore, this reaction can be considered completely reversible and its properties do not decline with the passage of time if the medium in which it takes place is free of impurities, especially CO2.

Many researchers have studied the possibility of improving the reaction specifications in terms of speed and temperatures by adding some materials to calcium hydroxide. Potassium nitrate KNO3 was added to calcium hydroxide (Shkatulov et al., 2015). This addition led to an improvement in the reaction rate and a decrease in the drying temperature by 5 to 10 °C. The addition of lithium and magnesium to calcium hydroxide led to an increase in the reaction rate (Yan et al., 2014).

Various designs of the reaction chamber have been developed with the aim that these designs are suitable for use in concentrated solar power plants.

The fixed bed reactor is characterized by ease and speed of control, however, the combination of reaction and energy storage place in one area makes the size of the reactor the most important factor in determining both power and storage capacity, and this leads to the invalidity of this type of reactor for storing thermal energy in concentrated solar power plants Where there is a need to store large amounts of thermal energy (Schmidt, 2017). In contrary, the moved bed reactor is characterized by the separation between the reaction area and the storage area for both calcium oxide and calcium hydroxide. Calcium oxide is present in tank A subjected to ambient conditions of temperature and atmospheric pressure. In order to obtain a certain amount of energy, an appropriate amount of calcium oxide is withdrawn and passed into the reactor, where water vapor is pumped in appropriate conditions for the reaction, so calcium hydroxide is formed, which is pumped to tank B and heat energy is generated. In the case of charging, the previous process is done in reverse.

The total energy that can be stored in the previous process is related only to the size of tanks A and B. The method of reactor design, its size and the speed of materials passing through it affects the power and allows it to be controlled precisely while maintaining low construction and operating costs (Ramm, 2013). In the fixed bed reactor, the solid reaction materials remain fixed in place, in contrast to the moved bed reactor, where these materials move between tanks A and B, hence the difference in naming between the two reactors.

In (Mejia et al., 2020), a cylindrical moving bed reactor was designed that includes 22 vertical tubes, each 18 mm in diameter and 330 mm in length, through which solid and gaseous reactants pass through, while the heating process is carried out by air (HTF), which enters from a hole at the bottom of the reactor cylinder and exits from a corresponding orifice at the top of the cylinder. This reactor was tested using calcium hydroxide macro-granules coated with aluminum oxide nanoparticles, and 6 charging and discharging cycles were performed on the same amount of material. The reactor showed good performance with charge and discharge efficiency close to 100 percent and the nanosphere maintained its strength.

2. Suggested method

Most of the published research on the $CaO/Ca(OH)_2$ storage system aims to use this system to store thermal energy in concentrated solar power plants, where it is necessary to recover the stored energy at the highest possible temperature in order to obtain a high yield in the turbines that generate electricity. For this reason, water in the gaseous state (steam) must be used in the exothermic reaction with CaO. The aim of this work is to take advantage of the mentioned storage system for domestic purposes such as space and water heating, and here the need for high temperatures is eliminated, which means a great simplification of the heat giving reaction, as water can be used in its liquid state instead of water vapor.

Figure 1 shows the energy changes in the storage and release process of the system $CaO/Ca(OH)_2$ at a regular atmospheric pressure of 1 bar. If we use calcium hydroxide at a temperature of 25 °C, we need 54 kJ to raise the

temperature of one mole to 510 °C, which is the temperature needed to disintegrate into calcium oxide and water. After reaching that temperature, each mole needs 94.6 kJ to complete the dissociation process, where we get one mole of water vapor and one mole of calcium oxide at a temperature of 510 °C. By moving to a temperature of 25 °C, water vapor turns into a liquid and loses 61.5 kJ, while calcium oxide remains in its solid state, but loses 23.5 kJ in the sensible form.
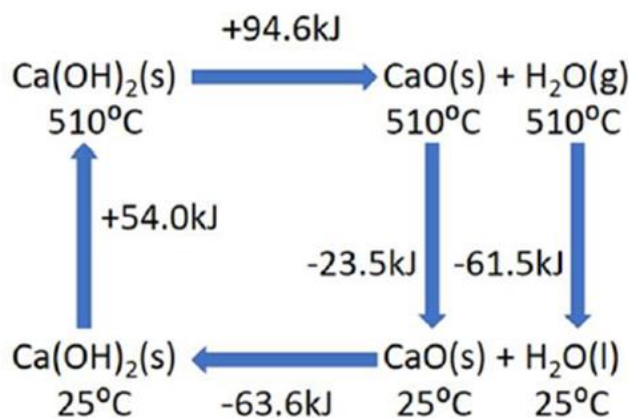

Figure 1: Energy stored and released in the system CaO/Ca(OH)$_2$ (Takham et al., 2018)

It is clear from Figure 1 that we need 148.6 kilojoules to decompose one mole of calcium hydroxide at a temperature of 25 °C, and as a result we get one mole of calcium oxide at the same temperature with a stored chemical energy of 63.6 kilojoules, or about 43% of the total energy that was entered into the reaction.

The method proposed in this work for using the system CaO/Ca(OH)$_2$ for domestic heating purposes can be summarized in the following points:

- Using concentrated solar power plants to convert calcium hydroxide into calcium oxide.
- Transporting and distributing the produced calcium oxide to the places of use.
- Production of thermal energy in places that require it by hydrating calcium oxide using water in a liquid state.
- Transporting calcium hydroxide to the solar power plants to convert it back into calcium oxide.

2.1 using of concentrating solar power plants to dry calcium hydroxide

In a tower solar station, thousands of mirrors direct the sun's rays to a receiver located at the top of the station's tower. The working fluid passes through this receiver. In many stations, it is a molten nitrate salt (Glatzmaier, 2011), where its temperature rises to 565 °C. The high temperature of the molten nitrate salt makes it suitable for use in drying calcium hydroxide as the required temperature is at least 510°C at atmospheric pressure of 1 bar

This drying process can use a moved bed reactor, where calcium hydroxide is passed through tubes in direct contact with the working fluid stream (HTF), in this case molten nitrate salt, which leads to the dissolution of calcium hydroxide to calcium oxide and water vapor. The amount that can be obtained from calcium oxide in this way depends on the capacity of the thermal station. If we assume that the heat capacity of the station is 10 MW, then we can theoretically obtain a chemical energy stored in calcium oxide of 4.3 MWh, which is equivalent to 13.6 tons CaO within one hour of solar brightness. The amount of water vapor resulting from the reaction that can be condensed into distilled water is 4.3 tons. The thermal energy that has not been converted into chemical energy, which is 5.7 MWh, can be used to heat the calcium hydroxide before it enters the moved bed reactor, which contributes to increasing the amount of calcium oxide that can be obtained.
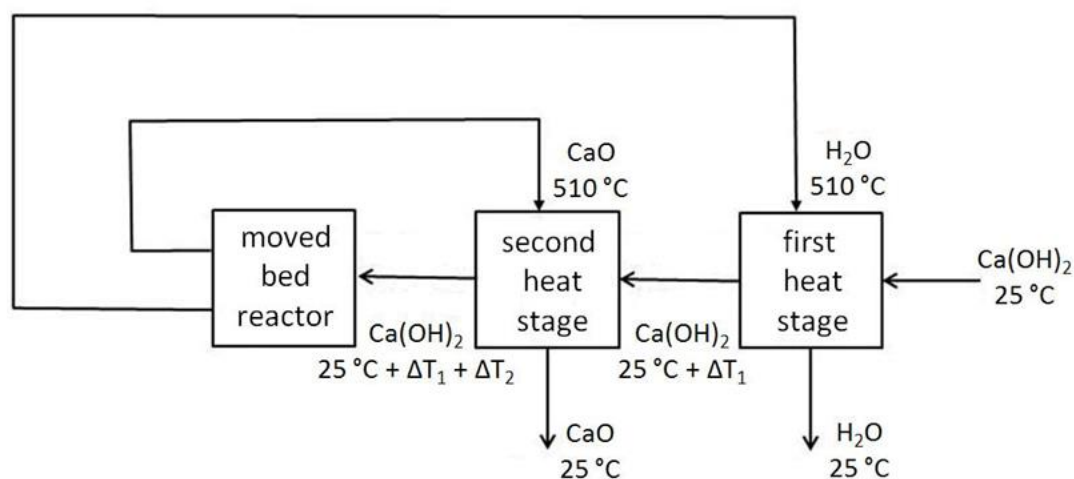
Figure 2: Box diagram of the drying of calcium hydroxide with utilization of the sensible and latent thermal energy of the resulting water vapor and calcium oxide.

Figure 2 shows in a simplified form the proposed stages of drying calcium hydroxide, taking advantage of the sensible and latent thermal energy of water vapor and the sensible thermal energy of the resulting calcium oxide. Calcium hydroxide, which is present at ambient temperature (25 °C), enters the first heating stage, where the thermal energy of water vapor resulting from the dissolution of previous amounts of calcium hydroxide is utilized. The temperature of calcium hydroxide after passing the first stage increases by $\Delta T1$. If we take into account that the amount of calcium hydroxide that enters the first stage of heating is about three times greater than the amount of water vapor that enters this stage, and if we also take into account that it is only possible to benefit from the potential energy of water vapor when it is transformed from the gaseous state to the liquid state At 100 °C, then $\Delta T1$ will be about 75 °C and the temperature of the calcium hydroxide after the first stage of heating will be about 100 °C.

In the second heating stage, the amount of calcium hydroxide (temperature close to 100 °C) is about 1.3 the amount of calcium oxide whose temperature is about 510 °C and therefore the temperature of calcium hydroxide is about 280 °C when it enters the moved bed reactor. The first and second heating stages resulted in saving 25 kJ per mole of calcium hydroxide (Fig. 1) and therefore the amount of thermal energy that is converted into chemically stored energy increases by 10% from 43% to 53% as a result of using thermal energy of the water vapor and calcium oxide produced by Calcium hydroxide drying.

2.2 Calcium oxide hydration using liquid water

Space and water heating processes for domestic purposes require relatively low temperatures (less than 80°C) compared to the temperatures required in electric power plants using concentrated solar energy. For this reason, the hydration of calcium oxide can be achieved using water in a liquid state where the required temperatures can easily be obtained. The hydration process can be performed automatically or simply manually, depending on the capacity to be secured. If the required power is large enough to be sufficient to heat a building, for example, then the automated method must be used here because the quantities that are consumed of calcium oxide are large. For example, securing a capacity of 100 kW (heating a residential tower) for one hour means that the energy consumed is 100 kWh. That is 360 MJ and this is equivalent to the chemical energy stored in 317 kg of calcium oxide, which is a large amount that can only be dealt with automatically.
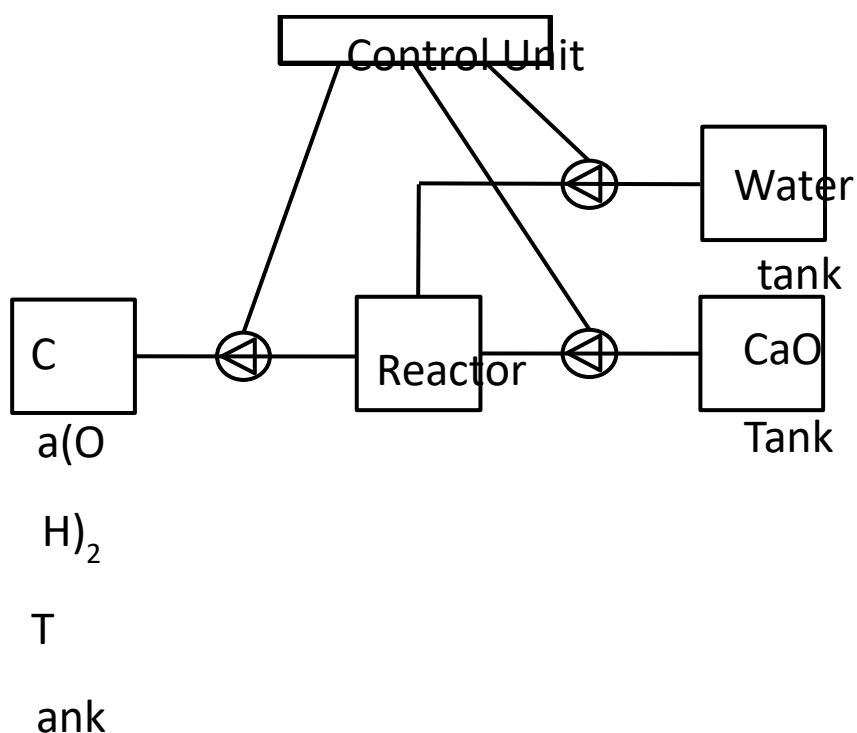
Figure 3: Box diagram of the hydration of calcium oxide by an automated method.

Figure 3 shows the box diagram of automated calcium oxide hydration. This scheme includes a water tank, a CaO tank, a $Ca(OH)_2$ tank, in addition to the reaction chamber, the control unit, and three pumps to provide input and output to and from the reaction chamber. The size of the tanks must be proportional to the capacity to be secured and the time interval between two consecutive fillings. The control unit regulates the flow of water and calcium oxide into the reaction chamber and calcium hydroxide from the reaction chamber into the tank. The reaction chamber must be equipped with a heat exchanger to transfer the resulting heat to the places of use.

3. Experimental results

The objectives of the conducted experiments in this work are as follows:

- Determination of CaO percentage in the used commercial calcium oxide powder.
- Determining the effect of the ratio between water and calcium oxide on the produced thermal energy and the temperatures that can be obtained.
- Determining the percentage of calcium oxide recovery from calcium hydroxide using a fixed focus solar concentrator.

An Omega SF-400 scale was used. Its screen has a resolution of 1 gram, so there is a measurement error of up to 0.5 grams due to the gram rounding process. The hydration experiments were carried out in a stainless steel chamber with a thickness of 2 mm, a diameter of 5.5 cm and a height of 7 cm. The chamber was isolated with a layer of 1 cm thickness insulation material from all sides. An EXTECH SDL 200 thermometer and logger was used to measure and record temperatures during the hydration process. The K-type sensor was placed between the foam insulation layer and the stainless steel material at the bottom of the reaction chamber.

Five experiments were carried out for reactions between commercial calcium oxide powder and water according to reaction (1). The molar mass of calcium oxide CaO is 56 grams, while the molar mass of water is 18 grams, so the ratio between the two substances in the previous reaction is 3.11.

In each of the five reactions 20 g of commercial powder and 40 g of water were used. After the reaction was performed, the reaction product was heated on an electric heater at low temperatures (about 100 °C) in order to get rid of the excess water as $Ca(OH)_2$ does not disintegrate except at temperatures exceeding 500°C. The reaction product was then weighed after removing the excess water. The difference between the weight we

obtain and the weight of the commercial powder used in the reaction represents the amount of water that reacted with the calcium oxide.

The weight of the water that was determined in the previous method was 5 g in each of the five reactions. Therefore, the amount of CaO involved in the reaction is 5 * 3.11 = 15.55 g, meaning that the percentage of calcium oxide in the powder used is 78%. If we take into account that the error rate of the scale is ±0.5 grams, this means that the percentage of calcium oxide in the powder used ranges between 70% and 86%.

Three experiments were conducted in which the amount of water (40 g) was kept constant, while the amount of calcium oxide was changed, where it was in the first experiment 20 g, in the second 15 g, and in the third 10 g. Figure 4 shows the difference between the resulting temperatures in the three reactions and the initial temperature ΔT as a function of time. It is clear from the figure that the amount of CaO greatly affects the maximum value of ΔT, as it reached in the first experiment 55.4 °C, in the second experiment 41.8 °C, and in the last experiment 30.5 °C.
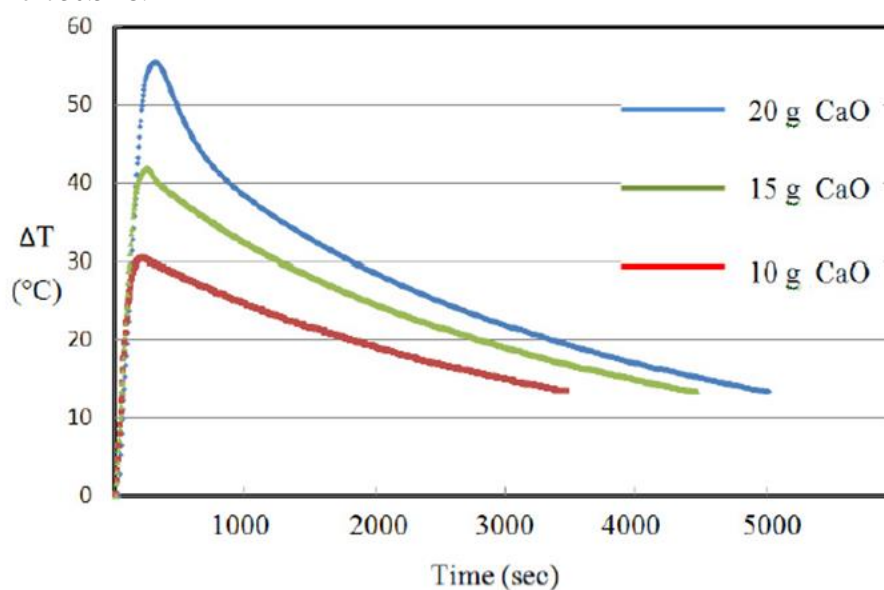

Figure 4: Effect of CaO amount on temperature rise

Figure 5 shows the maximum value of ΔT as a function of the amount of calcium oxide used. It is clear from the figure that there is a linear proportionality between these two values and therefore the maximum resulting temperature can be controlled by controlling the amount of calcium oxide used.
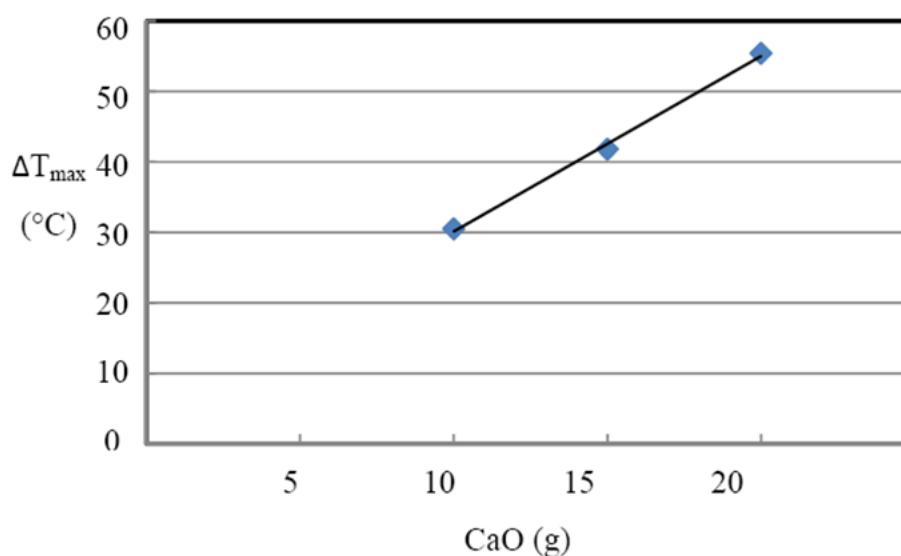

Figure 5: Effect of the amount of CaO on the maximum rise in temperature

A fixed focus solar concentrator was used to dry the calcium hydroxide produced by calcium oxide hydration (Fig. 6). The solar dish used in this concentrator has an area of 2 m² and the diameter of the focal spot is 10 cm. Ten experiments were carried out for drying calcium hydroxide. The experiments were carried out according to the following steps:

[1]. Hydration of 20 g of calcium oxide in 40 g of liquid water at room temperature and using the previously described isolated reaction chamber.

[2]. On the next day, the reaction chamber is placed after removing the insulation in the focus of the solar concentrator in Midday for one hour.

[3]. The Chamber is left to cool down and then weighed to ensure that the amount of water used for hydration was completely evaporated (within the accuracy of the scale).

[4]. We return to the first step using the same material in the reaction chamber for the next cycle.

Figure 6: Photograph of the concentrator used to dry calcium hydroxide.

Figure 7 shows the temperature T recorded during the first hydration process and the difference ΔT between the recorded temperature and the initial temperature T_i, which was 29.1 °C. The maximum recorded temperature ,84.6 °C, was reached 280 seconds after the start of the reaction. The difference between the recorded maximum temperature and the initial temperature is 55.5 °C. The temperature decreases with time, reaching 42.5°C after 5,000 seconds, which is 13.4°C more than the initial temperature. We note that the decrease in temperature after reaching the peak is slow, and the reason for this is the presence of foam insulation. However, if we want to speed up the decrease, the insulation must be removed, which leads to a faster transfer of thermal energy from the reaction chamber to the surrounding medium.

The maximum difference ΔT_{max} between the recorded temperatures and the initial temperature in each of the ten experiments carried out, ranges between 53.4 and 56.2 degrees Celsius. These, small discrepancies between ΔT_{max} values can be attributed to measurement errors and random inhomogeneities in the calcium oxide concentration within the powder used in the experiments.

The most important result that can be reached from the previous ten experiments is the possibility of complete drying of calcium hydroxide and obtaining the initial amount of calcium oxide using concentrated solar energy repeatedly and without any decline in the properties of the resulting calcium oxide.
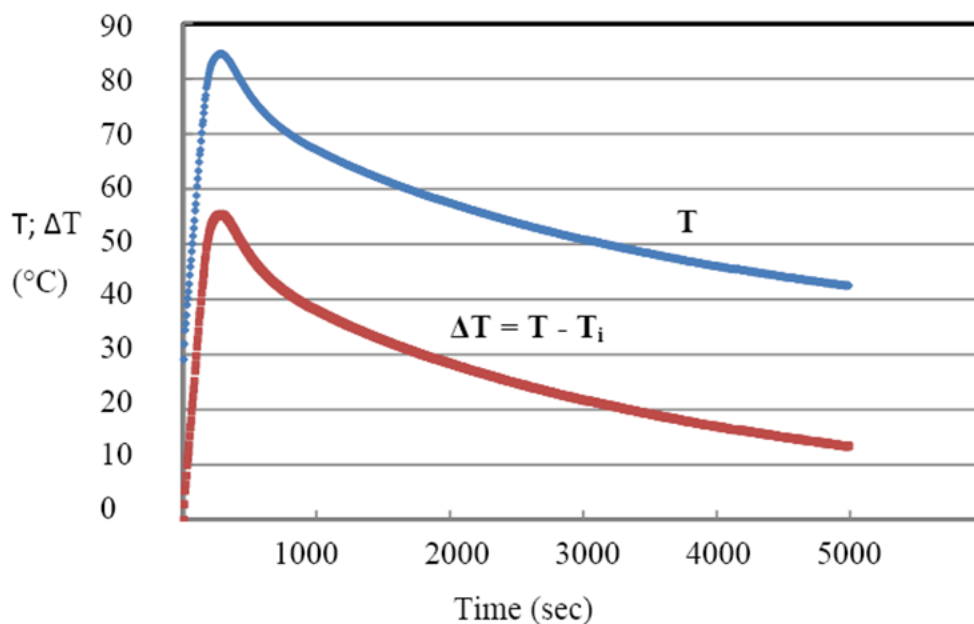
Figure 7: Temperature (T) recorded during hydration

4. Conclusion

In this work, the possibility of using the thermal energy storage system $CaO/Ca(OH)_2$ in domestic applications such as space heating and heating was studied. The proposed method is based on the use of concentrating solar power plants with high thermal capacities to dry calcium hydroxide and provide consumers with the resulting calcium oxide. Thermal energy is obtained by the consumer by using water in the liquid state to hydrate calcium oxide, which leads to the release of thermal energy at temperatures suitable for domestic uses. Ten experiments were conducted on the hydration and drying cycle of the $CaO/Ca(OH)_2$ storage system, and a fixed focus solar concentrator was used in the drying process. The experimental results showed the possibility of drying calcium hydroxide and converting it to calcium oxide completely without any change in the specifications. The hydration experiments also showed the possibility of controlling the resulting temperatures by changing the ratio between water and calcium oxide.

Acknowledgment

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