

Editorial

Thermochemical Energy Storage Based on Carbonates: A Brief Overview

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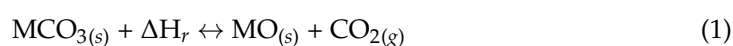
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Energy storage is becoming one of the main challenges facing the massive integration of Variable Renewable Energy (VRE) in the coming years. Solar Photovoltaics (PVs) and wind plants are undergoing enormous development, and they are leading the transition to a renewable energy mix. Given its intrinsic variable nature, a huge need for energy storage is expected in the coming decades. Efficient, cost-effective, and scalable energy storage systems stand as one of the main technological challenges for the massive deployment of renewable energies.

High-temperature Thermal Energy Storage (TES) systems have undergone great synergistic development together with Concentrating Solar Power (CSP) plants, although the potential of TES includes integration with other types of technologies, such as Pumped Thermal Energy Storage (PTES) or even their integration to store electrical energy. The market for high-temperature thermal storage is largely led by molten salt-based systems. Despite its maturity and acceptable performance, molten salt energy storage presents several drawbacks, related to corrosiveness, limitation of the maximum working temperature to avoid salt degradation (which limits the efficiency of the power cycle), limitation of the minimum working temperature to avoid salt solidification, as well as an elevated cost (~USD 900/ton). Thermochemical Energy Storage (TCES) is an attractive alternative to molten salt systems.

TCES is based on reversible chemical reactions. Energy is provided (storage step) to carry out an endothermic reaction, and, once this has taken place, the products are stored. When energy is demanded, the stored materials are promoted to react according to the reverse reaction (exothermic), releasing in this way the stored energy. Among the potential TCES, the metal carbonate-based system is one of the most promising alternatives due to its high-turning temperature, high-energy density, and usually the low price of the raw materials. The most well-established system is the one based on calcium carbonate (CaCO₃/CaO), in the so-called Calcium-Looping (CaL) process [1], although there are other interesting alternatives based on barium carbonate [2], strontium carbonate [3] or magnesium carbonate [4].

Figure 1 shows the conceptual scheme for a TCES based on carbonates. Carbonates decomposed through the endothermic calcination reaction (Equation (1)), where M generically represents Ca, Sr, Ba, etc. Calcination takes place in a solid–gas reactor, usually under near-to-ambient pressure. Most of the previous research proposed Fluidized Bed (FB) reactors due to their maturity and the high mass and heat transfer provided, although Entrained Flow (EF) reactors could be a promising alternative for the use of fine particles. The reaction temperature depends on the equilibrium CO₂ partial pressure, also conditioning the temperature of the heat to be stored (i.e., CSP). Once calcination occurs, CO₂ and the metal oxide are stored separately after passing through a Heat Exchanger Network (HEN) to reduce its storage temperature. The CO₂ is compressed usually up to liquid state to reduce the storage volume.



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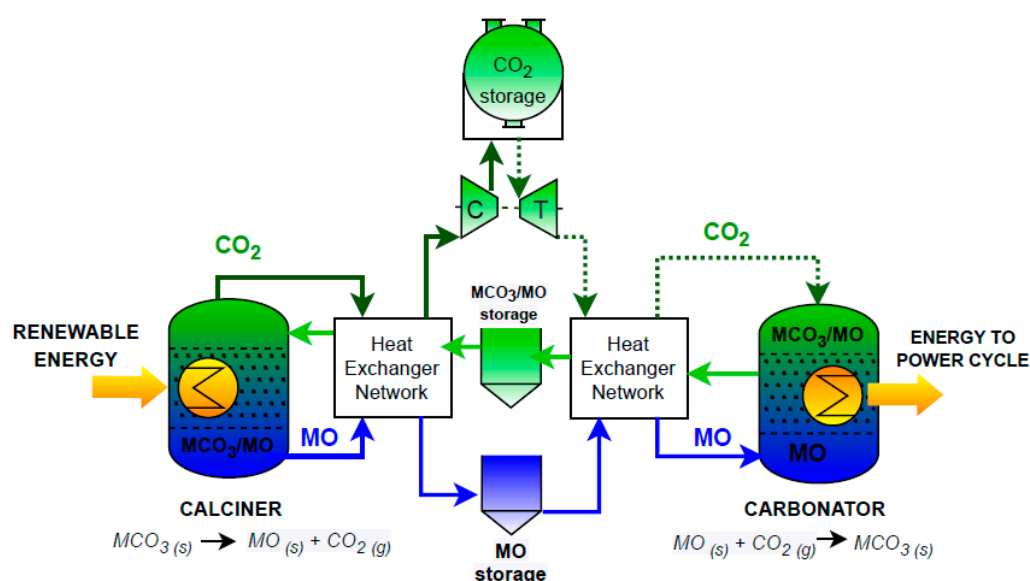


Figure 1. Carbonate-based TCES conceptual scheme. Adapted from [5].

When energy is demanded, the metal oxide and CO_2 stored are sent to the carbonator (another gas–solid reactor) where carbonation occurs, releasing the stored energy for electricity production through a power cycle. Carbonation temperature is also conditioned by the CO_2 equilibrium pressure. Importantly, the higher the carbonation temperature, the higher the temperature heat to be provided to the power cycle, increasing the thermal-to-electric efficiency.

Metal carbonates are promising materials due to several key advantages:

- Carbonate systems have a high theoretical energy density, which allows for maximizing the storage capacity. It is worth highlighting, in this case, the systems based on CaCO_3/CaO , SrCO_3/SrO and MgCO_3/MgO ($\sim 3\text{--}4 \text{ GJ/m}^3$). These values are ~ 10 times higher than sensible heat storage systems (i.e., molten salts); despite this, it must be considered that the systems are more complex, requiring tanks for the storage of products (solid and gas/liquid). Thus, the real energy density of carbonate TCES systems depends on material properties, reaction efficiency and process configuration [6].
- Carbonates are widely available, usually cheap, and environmentally friendly. Calcium carbonate stands out, one of the most abundant materials on the planet, and with a large-scale price of around EUR 10/ton (two orders of magnitude lower than the price of solar salts).
- A key advantage over molten salt systems is the ability to store products at ambient temperature, which significantly reduces electricity consumption and eliminates the risks derived from the solidification of salts. This makes the system more flexible, increasing the energy storage capacity in days or even weeks, although it also increases the complexity of the heat exchangers network when it comes to recovering the sensible heat of the materials at the exit of the endothermic reactor (high temperature).
- Several carbonates have a high-turning temperature, which gives them the ability to release heat through the exothermic reaction at temperatures higher than 900°C and, therefore, the possibility of integrating with high-efficiency power cycles, such as combined cycles, supercritical Rankine cycles or Brayton Cycles. They stand out: SrCO_3 , BaCO_3 , PbCO_3 and CaCO_3 .
- Regarding the materials and equipment, carbonate TCES is based on solid–gas reactions, which gives the system an extra degree of complexity compared to systems based on sensible heat. Nevertheless, in the case of CaCO_3/CaO TCES, there is a closeness with the cement industry (reactors, vessels, cyclones, etc.), which facilitates the deployment of the technology.

The renewables-driven calciner is the main challenge of the technology. In addition, the handling of high-temperature solids must also be investigated in detail when scaling up the technology. Problems, such as material agglomeration, could compromise the plant operation. Another challenge in the case of TCES carbonates is the progressive deactivation of the sorbent until reaching a residual conversion value, which limits the heat released in the exothermic carbonation reaction. This fact is mainly affected by the phenomenon of pore plugging and the significant sintering taking places at very high temperatures ($>900\text{ }^{\circ}\text{C}$). The residual sorbent conversion mainly depends on the sorbent precursor properties, particle size and the process conditions (temperature, pressure and atmosphere composition in the reactors) [7]. To overcome this challenge, a large number of alternative sorbents, synthetics (i.e., CaO/SiO_2 [8]) or natural (i.e., dolomite) and milder calcination conditions (with the reactions occurring in CO_2 -diluted atmosphere) are being proposed [1].

In addition to the important advantages described above, carbonate TCESs have market opportunities that could boost their development in the coming years. Carbonate TCESs have been usually linked to CSP plants due to their inherent integration potential, but these systems could also be used for electricity storage from PV or wind facilities. The need to find solutions to store electricity on a large scale will have the potential to integrate these systems in photovoltaic plants from the introduction of electrical resistances in the calciner, providing the necessary energy for the calcination. Another opportunity is the huge potential of carbonates as a post-combustion CO_2 capture system. The CaL process was first proposed for CO_2 capture. The CaL process for CO_2 capture, which is essentially the same process that, for TCES, is currently close to the commercialization stage (TRL7). The commercial development of these CO_2 capture systems could pave the way for the development of carbonate-based TCES, due to the knowledge acquired in the implantation of the systems and the economy of scale.

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Conflicts of Interest: The author declares no conflict of interest.

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