Thermodynamic analysis of a magnesium carbonate thermochemistry and compressed air energy storage system

by
Eric R. Rebarchik

A THESIS

submitted to

Oregon State University

Honors College

in partial fulfillment of
the requirements for the
degree of

Honors Baccalaureate of Science in Chemical Engineering
(Honors Scholar)

Presented August 19, 2022
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Nick AuYeung

In this work, a hybrid thermochemistry compressed air energy storage (CAES) system is investigated. Following a review on chemical reactions investigated for use in thermochemical energy storage (TCES) systems, from these chemistries, the conversion of magnesium carbonate, MgCO$_3$, to magnesium oxide, MgO, and carbon dioxide, CO$_2$, was further analyzed for use in an indirect heat transfer system in conjunction with CAES. A mathematical model was constructed to simulate a steady-state CAES and chemical reactor system which uses hydrostatic compensation technology developed by Hydrostor Inc. to maintain constant pressure throughout operation. The model consists of the following components: 1) compressors; 2) a chemical reactor; 3) a packed bed for sensible heat storage (SHS); and 4) a turbine to generate power. The model indicates the advantages of using TCES appear during long storage durations and when the SHS wall overall heat transfer coefficient is increased. Energy remains trapped in the chemical bonds of the TCES material, whereas it can be lost to the surrounding environment when using SHS. For short storage periods where SHS can be well-insulated, the costs of using TCES will likely outweigh any benefits.

Keywords: Magnesium carbonate, magnesium oxide, thermochemical energy storage, compressed air energy storage, indirect heat exchanger

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I understand that my project will become part of the permanent collection of Oregon State University, Honors College. My signature below authorizes release of my project to any reader upon request.

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1. Introduction

Sustainable energy sources such as solar and wind are inherently dependent on intermittent weather and climate conditions and on their own are not reliable enough to meet current grid-scale demand consistently. During conventional electrical power generation, any energy that is not consumed immediately is wasted\cite{1}. In the case of intermittent energy sources, the periods during which electrical power is produced do not always align with periods of high energy demand, causing usable energy to be lost. When renewable energy sources are not available to meet demand, the burning of fossil fuels (e.g. gas-fired peaking plants) is commonly used to generate electricity, releasing greenhouse gases\cite{2}. Energy storage technologies can provide stability in the power grid by storing energy during periods of low energy demand which can be drawn upon during more demanding times. Electrical energy generated by intermittent sources can be converted to other forms of energy and later used to provide a steady source of power. Some of the most common energy storage technologies are pumped hydroelectricity storage, batteries, and fuel cells, each with their own advantages and weaknesses\cite{1}. No single energy storage technology can meet requirements for renewable energy integration or mitigation of intermittency in the power utility sector, making advancements and constant discovery important to meeting the energy demands of the future\cite{1}.

Among these technologies, compressed air energy storage (CAES) has many notable advantages for storing renewable energy, including a long lifetime and economic competitiveness \cite{3,4}. During a typical CAES process, ambient air is compressed using excess energy from renewable sources during a period of low energy demand. After a charging period, the compressed air is stored in an underground vessel or cavern for a period ranging from hours to days. When energy is needed, the compressed air is heated using the combustion of natural gas and led through turbines to generate power. The use of natural gas emits greenhouse gases and increases the operating costs of the plant. Traditional CAES systems suffer from low energy efficiencies, less than 50%, due to waste of compression heat\cite{5}.

To avoid the release of greenhouse gas emissions, the use of an advanced adiabatic compressed air energy storage (A-CAES) has been proposed, which stores the thermal energy of the compressed air during the charging step of the process and releases it during discharge. During the charging step of an A-CAES system, the hot compressed air passes through an energy storage system, such as a packed bed for sensible heat storage (SHS) or phase change material for latent heat storage (LHS), and energy from the hot air is transferred to the energy storage media. The energy storage system is well insulated to prevent heat losses to the surrounding environment, therefore storing thermal energy that can be returned to the air later. During discharge, the air is released through the same energy storage system to be reheated before passing through turbines. The additional energy stored during A-CAES reduces or possibly even negates the need for burning natural gas to reheat air before it enters a turbine. A round-trip efficiency of 70% is considered to be the goal for A-CAES plants, though round trip efficiencies of 72-75% have been predicted with the use of models\cite{5,6}.

Extending upon this, Hydrostor Inc., a Canada-based energy storage company, has designed a unique modification to the traditional A-CAES energy storage system design to increase overall storage efficiency further. The Hydrostor A-CAES system
uses a reservoir filled with water connected to specially designed caverns for compressed air storage\textsuperscript{[7]}. During the charging step of the Hydrostor energy storage system, the compressed air is moved through a system to store thermal energy and into the storage caverns\textsuperscript{[7]}. During this process, the compressed air displaces water upward into the reservoir, which is analogous to parts of a pumped hydro facility and allows the plant to operate at a constant pressure below ground\textsuperscript{[8]}. The displacement of the water upwards increases the hydrostatic pressure exerted back into the cavern as the pressure from the incoming air increases. During discharge, the water is allowed to flow back into the cavern as air is pushed to the surface by hydrostatic pressure, through the thermal energy storage system, and through a turbine.

The addition of the water reservoir used for hydrostatic compensation and its ability to maintain a constant pressure throughout plant operation allows for equipment that handles the air, such as the compressors and turbines, to run at nearly constant conditions\textsuperscript{[8]}. Typical CAES plants operate under transient conditions, with pressure in the storage vessel increasing as air is compressed and moved into it with the reverse occurring during discharge. The constant conditions of the Hydrostor system improve the efficiency of the equipment, therefore increasing the overall efficiency of the energy storage process.

Thermochemical energy storage (TCES) has gained recent attention for its potential use in the storage of renewable energy, due to several notable advantages. Generally, TCES systems store energy through a charging step that uses an endothermic reaction to store energy in chemical bonds. The discharging step consists of an exothermic reaction to release energy when needed. A general TCES reaction may be represented by the following chemical equation:

\[ A + \Delta H \leftrightarrow B + C \]  

(1)

Where A is the TCES material before charging, which after adding energy, \( \Delta H \), becomes the products B and C. To control when the reverse reaction occurs, it is convenient for B to be solid and C to be in the gas phase. If the reaction used to store energy is reversible, the stored energy can be entirely recovered. Additionally, storage inefficiencies associated with heat loss are not a concern and the energy storage density of TCES materials is high when compared with SHS and LHS systems\textsuperscript{[11]}. The advantages associated with TCES have the potential to improve CAES system efficiency, so identifying TCES reactions to store energy from hot, compressed air has been the focus of research efforts over the past several decades\textsuperscript{[6],[9],[10]}. The current work aims to build on the achievements of this research by identifying chemical reactions that could be implemented into future CAES systems.

2. Methods

To identify an optimum reaction for the storage of sensible heat from compressed air, literature on thermochemical energy storage was reviewed to select a reaction with the following desirable attributes: 1) The reaction must occur at achievable operating conditions using the compression of air from ambient temperature (i.e. roughly 400-600°C); 2) Product separation must be achievable following the storage of energy so the discharge reaction can be controlled; and 3) The enthalpy of
the reaction must be great enough to significantly heat the air during discharge. The types of TCES reactions considered and important conclusions are summarized, and the model used for the simulation of the chosen chemistry in a CAES system is described in the following sections.

2.1 Metal Oxides

Metal oxide redox reactions have gained attention for TCES applications due to high operating temperatures, the ability to use oxygen in air as a reactant and heat transfer medium, and simple product separation due to solid-gas reactions\textsuperscript{6,11,12}. The BaO\textsubscript{2}/BaO redox system has been considered for integration into an A-CAES system due to its moderate heat storage capacity, low material costs, and a moderate turning temperature, although there are notable challenges associated with the material\textsuperscript{6}. In the presence of any moisture and CO\textsubscript{2}, an undesirable reaction will occur with BaO\textsubscript{2}, which necessitates the use of a system to dry air if direct heat transfer is used during CAES. Additionally, the operating temperature required to use the BaO\textsubscript{2}/BaO system for TCES is relatively high compared to temperatures reachable by compressing air to typical CAES pressures, and the reaction suffers from poor reversibility\textsuperscript{11}. Other metal oxide redox systems were considered but disregarded due to similar issues and material toxicity. Ultimately, these challenges led to the search for other chemical reactions for use in a hybrid TCES and A-CAES system.

2.2 Perovskites

Perovskite oxides are materials described by the formula ABO\textsubscript{3-δ}, where A and B are both cations. The structure of perovskites remains stable over large temperature ranges, with oxygen able to move in and out of the lattice formed by the cations\textsuperscript{13}. By reacting with oxygen, perovskites may exhibit large changes in oxygen non-stoichiometry which are associated with energy change as the structures partially oxidize and reduce. The enthalpies of reaction associated with these perovskite reactions are generally lower than enthalpies of reaction of other TCES candidates, such as metal oxides, due to only partial stoichiometric oxidation and reduction. Importantly, the choice of A and B site cations, oxidation state of the cations, and the ionic radii affect the structure and properties of perovskite material, enabling tailoring for specific purposes and operating conditions. Research on the use of perovskites in TCES applications is a growing area of interest, with particular focus on using machine learning algorithms to identify potential candidates for synthesis and experimentation\textsuperscript{14,15}. As advancements in the use of machine learning for chemical discovery are made, the use of perovskites for implementation into an A-CAES system should be investigated.

2.3 Hydroxides

Alkaline earth metal hydroxide reaction pairs have also been considered for energy storage applications\textsuperscript{16,17}. Like many of the metal oxide redox reactions considered, the turning temperatures of the Ca(OH)\textsubscript{2}/CaO and Sr(OH)\textsubscript{2}/SrO systems are higher than desired for a CAES system. However, the turning temperature of the Mg(OH)\textsubscript{2}/MgO reaction is within the desired range for use with CAES. Experimental results indicate the Mg(OH)\textsubscript{2}/MgO chemical energy storage system is inefficient at
dehydration temperatures lower than 350˚C and higher than 500˚C, because below this range the Mg(OH)$_2$ dehydration reaction occurs slowly, and above this range sintering of the energy storage material occurs$^{[18]}$. The operating temperatures of Mg(OH)$_2$ and its high availability make it a promising candidate for implementation with A-CAES. However, the exothermic reaction during discharge requires the addition of water vapor as a reactant. This would require water to either be stored in the gas phase or generated by vaporizing water. The standard enthalpy of the Mg(OH)$_2$/MgO reaction with liquid water (37.5 kJ/mol) is significantly lower than the enthalpy of the reaction with water vapor (80.5 kJ/mol), which would result in a net loss in efficiency if the water could not be stored in the vapor phase. This would require storage equipment designed to keep pressures low enough to keep water in the vapor phase or well insulated enough to not condense. Due to this additional challenge, a different TCES reaction was considered.

2.4 Carbonates
Carbonate reactions are promising for TCES applications due to their high turning temperature, high energy density, and low price of raw materials$^{[19]}$. However, many of the most studied carbonate reactions, including CaCO$_3$/CaO and SrCO$_3$/SrO, have turning temperatures of greater than 900˚C at ambient pressure, making them unideal for use with CAES$^{[19]}$. The reaction of the MgCO$_3$/MgO system, like with Mg(OH)$_2$, occurs at a much lower temperature (396 ˚C). Studies that assess MgCO$_3$ for use as a TCES material are not as abundant as for carbonates with higher turning temperatures, but research is being done on how to improve storage efficiency$^{[18]}$. Due to its low turning temperature and gaseous product that will not undergo a phase change at ambient conditions, the MgCO$_3$/MgO reaction was selected for analysis with the A-CAES model. The reaction is represented by the following chemical equation:

\[
MgCO_3 + \Delta H \leftrightarrow MgO + CO_2; \Delta H = 100.7 \text{ kJ/mol}
\]  

(2)

2.5 CAES Model Description
To determine whether a chemical reaction could be suitable for TCES to supplement the overall storage efficiency of an A-CAES system, a thermodynamic model was constructed to consider the major sources of energy storage and loss in a basic A-CAES system. Energy and exergy analyses were performed in conjunction with a sensitivity analysis on model parameters to determine the conditions needed to maximize storage efficiency.

The system model (Figure 1) consisted of: 1) compressors; 2) a chemical reactor which uses indirect heat transfer to store thermal energy from the compressed air by driving the endothermic conversion of MgCO$_3$ to MgO and CO$_2$ during charging and the reverse, exothermic reaction during discharge; 3) a packed bed for SHS of thermal energy from the air, and; 4) a turbine to generate power. Air was assumed to behave as an ideal gas. In the charging step, energy from renewable energy sources during a period of low energy demand is used to compress air, resulting in the heating of the air. The air stream then moves through a chemical reactor in which a heat exchanger is used to allow for heat transfer between the hot air and TCES material. The air and TCES material remain in separate chambers, allowing indirect heat transfer to take place without the air affecting the TCES chemical reaction. Thermal energy from the
air transfers to the TCES material and the system approaches thermodynamic equilibrium along its length. The energy drives the endothermic reaction of MgCO$_3$ to form MgO and CO$_2$, storing the thermal energy from the air in chemical bonds. The CO$_2$ released during the exothermic reaction is off-gassed and stored until discharge. The air stream then passes through an SHS system consisting of a packed bed to store more thermal energy and then into a cavern (or other appropriate storage vessel). The air is stored in the cavern until a period of high energy demand. During discharge, the air stream is released from the cavern through where it entered, recovering energy from the SHS packed bed. The air stream then passes through the reactor, where CO$_2$ has been reintroduced on the TCES side and the exothermic reaction to reform MgCO$_3$ takes place. The energy released helps to warm the air further before the air stream enters a turbine for power generation.

![Diagram of the process]

**Figure 1.** Model overview (air travels clockwise through the system). During system charging, air is compressed from ambient conditions to storage pressure using energy from a renewable energy source, causing it to heat up. The compressed air moves through a TCES reactor, driving a reversible, endothermic reaction forward. The air moves through a SHS system before being stored. During discharge, the air reverses direction through the system. The air gains energy back from the SHS and reactants are added to the TCES reactor to cause an exothermic reaction to take place and heat the air further. The reheated air finally passes through a turbine to generate power. Stream temperatures are labeled $T_{1-6}$.

Several key assumptions were made to simplify calculations. Air was assumed to behave ideally for all calculations, with a molar heat capacity of 29.1 J/mol/K and ratio of specific heats of 1.4. Heat loss from the TCES reactor during charging and discharging operations was neglected, but heat loss was not neglected in the SHS system. The SHS wall overall heat transfer coefficient was assumed to be constant along the length of the packed bed.
The compression of air was assumed to be described by Eq. 3 and Eq. 4:

\[ \dot{W}_C = \dot{m} C_p T_1 \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} \eta_{C, poly}^{(k-1)} - 1 \]  
\[ T_2 = T_1 \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} \eta_{C, poly}^{(k-1)} \]  

Where the power used to compress air, \( \dot{W}_C \), is calculated for an ideal gas being compressed to storage pressure, \( P_2 \), from ambient temperature and pressure, \( T_1 \) and \( P_1 \), respectively. The molar heat capacity of air is represented by \( C_p \) and the mass flow rate of the air stream is represented by \( \dot{m} \). The polytropic efficiency of the compressor is given by \( \eta_{C, poly} \) with the ratio of specific heats for air being represented by \( k \). The temperature of the air leaving the compressor is represented by \( T_2 \). Similarly, the power generated by the turbine and final air stream temperature during discharge are calculated using Eq. 5 and Eq. 6:

\[ \dot{W}_T = \dot{m} C_p T_5 \left( 1 - \frac{P_6}{P_5} \right)^{\eta_{T, poly}^{(k-1)}} \]  
\[ T_6 = T_5 \left( \frac{P_6}{P_5} \right)^{\eta_{T, poly}^{(k-1)}} \]  

Where the power generated by the turbine, \( \dot{W}_T \), is calculated using the temperature \( T_5 \) and pressure \( P_5 \) at the turbine inlet and the pressure \( P_6 \) at the turbine outlet, ambient pressure. The polytropic efficiency of the turbine was represented by \( \eta_{T, poly} \).

The TCES component of the model was assumed to take place in a reactor through which indirect heat transfer can take place between the compressed air and TCES material. During the charging step, heat from the air is transferred to the MgCO\(_3\), which is initially at ambient temperature. The air heats the MgCO\(_3\) to above the turning temperature (397°C). Consequently, the heat from the air is used to drive the endothermic reaction represented by Eq. 2 forward to produce MgO and CO\(_2\). The compressed air, MgO, and CO\(_2\) in the reactor reach thermal equilibrium at a temperature higher than the turning temperature, and the compressed air passes into the SHS system. The MgO remains fixed in the reactor for storage, and the CO\(_2\) is off-gassed and stored for use during the discharging step.

The direction of compressed air flow is reversed during discharge, which causes it to flow through the SHS system and reactor again. The CO\(_2\) is reintroduced to the MgO, causing the reverse, exothermic reaction to occur. The compressed air is heated by the SHS system and then the exothermic reaction in the reactor before entering the turbine for power generation.
The energy balance for the SHS packed bed was approximated by using a 1-D model to represent a cylindrical packed bed with openings to the reactor and storage cavern. The model was based on previous research from Oregon State University with the following assumptions: 1) the temperature of the packed bed remains constant in the radial direction throughout operation; 2) heat transfer from radiation is negligible; 3) individual particles are uniform in temperature; 4) The heat loss to surroundings only occurs through air in the packed bed; 5) The mass flow rate through the packed bed remains constant; and 6) the velocity of air through the packed bed is uniform.

Fluid and solid phases are considered throughout the packed bed, with the general equations for the model being adapted from Lei et al. to consider heat accumulation, convective flux from incoming air, conduction, convective heat transfer between air and the SHS material, and heat loss from the packed bed to its surroundings. The material parameters used in the model are listed in Table 1.

Table 1. Material Parameters used in SHS model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat capacity of air</td>
<td>$C_{p,\text{air}}$</td>
<td>1050 J/(kg·K)</td>
</tr>
<tr>
<td>Thermal conductivity of air</td>
<td>$k_{\text{air}}$</td>
<td>0.0455 W/(m·K)</td>
</tr>
<tr>
<td>Viscosity of air</td>
<td>$\mu_{\text{air}}$</td>
<td>3.0×10⁻⁵ kg/((m·s))</td>
</tr>
<tr>
<td>Diameter of SHS material particles</td>
<td>$d_p$</td>
<td>0.02 m</td>
</tr>
<tr>
<td>Density of SHS material</td>
<td>$\rho_s$</td>
<td>2500 kg/m³</td>
</tr>
<tr>
<td>Heat Capacity of SHS material</td>
<td>$C_{p,s}$</td>
<td>830 J/(kg·K)</td>
</tr>
<tr>
<td>Thermal conductivity of SHS material</td>
<td>$k_s$</td>
<td>5.69 W/(m·K)</td>
</tr>
</tbody>
</table>

2.6 Energy Analysis

The primary value indicating TCES performance in the hybrid CAES model is the round-trip efficiency, defined as the ratio of the power output obtained from the turbine during discharge to the power put into the system during charging and storage. For a CAES system in which no additional power input is required following compression, the round-trip efficiency is expressed as follows:

$$RTE = \frac{W_T}{W_C} \times 100\%$$

(7)

Where $RTE$ represents the round-trip efficiency, $W_T$ represents the total power output of the turbine, and $W_C$ represents the total power input required to run the compressor for charging. For TCES to be worth implementing into a CAES system, the round-trip efficiency of the energy storage system must be higher than it would be with only SHS in use.

2.7 Sensitivity Analysis

A sensitivity analysis was performed, comparing the round-trip efficiency of an A-CAES system using an inert packed bed for SHS with the round-trip efficiency of an A-CAES system using both MgCO₃ TCES and SHS. For the analysis, baseline model parameters were chosen to be adjusted individually for the purpose of observing their impact on round-trip efficiency. The model parameters and adjustments made
during the sensitivity analysis are listed in Table 2. The parameters were selected to systematically test the impact changing system variables has on the round-trip efficiency of the energy storage. Baseline values were selected based on reasonable A-CAES operating conditions\cite{5,6}. The maximum storage pressure considered for the compressed air was 50 bar and storing energy for more than 48 hours at a time was not considered. The turning temperature of the chosen TCES reaction is 396°C (at ambient pressure) so reaction conditions for the charging and discharging of the system were set on either side of this threshold value. As the number of compressors used to reach the storage pressure increases, the compression process approaches isothermal behavior and the temperature increase associated with compression diminishes. The range of values for each parameter were chosen to reflect the limits of reasonable operating conditions.

Table 2. Sensitivity analysis parameters and corresponding changes investigated to determine impact on system round-trip efficiency. Each parameter and the changes investigated to each were modeled for a system with TCES and a system without TCES supplementing a packed bed for SHS.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Baseline Value</th>
<th>Change Investigated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Mass Flow Rate into System</td>
<td>0.25 kg/s</td>
<td>-20.0%, +20.0%</td>
</tr>
<tr>
<td>Air Mass Flow Rate Out of System</td>
<td>0.50 kg/s</td>
<td>-20.0%, +20.0%</td>
</tr>
<tr>
<td>Storage Pressure</td>
<td>40 bar</td>
<td>-25.0%, +25.0%</td>
</tr>
<tr>
<td>Charging Time</td>
<td>6 hrs</td>
<td>-33.3%, +33.3%</td>
</tr>
<tr>
<td>Idle Time</td>
<td>24 hrs</td>
<td>-95.8%, +200%</td>
</tr>
<tr>
<td>Charging Reaction Temperature</td>
<td>500°C</td>
<td>-6.5%, +6.5%</td>
</tr>
<tr>
<td>Discharging Reaction Temperature</td>
<td>350°C</td>
<td>-8.0%, +4.8%</td>
</tr>
<tr>
<td>Fraction of TCES Material Reacted</td>
<td>0.80</td>
<td>-25.0%, +25.0%</td>
</tr>
<tr>
<td>SHS Packed Bed Length</td>
<td>7.5 m</td>
<td>-33.3%, +33.3%</td>
</tr>
<tr>
<td>SHS Packed Bed Diameter</td>
<td>1.5 m</td>
<td>-33.3%, +33.3%</td>
</tr>
<tr>
<td>SHS Wall Overall Heat Transfer Coefficient</td>
<td>0.25 W/m²/K</td>
<td>-100%, +100%</td>
</tr>
<tr>
<td>Compressor Polytropic Efficiency</td>
<td>0.90</td>
<td>-11.1%, + 5.6%</td>
</tr>
<tr>
<td>Number of Compressors</td>
<td>3</td>
<td>-66.7%, + 66.7%</td>
</tr>
</tbody>
</table>

3. Results

Compared to values of CAES and A-CAES round trip efficiencies found in other works, the results provided by the model are greater than anticipated for the system with and without TCES implementation. Using the baseline values recorded in Table 2, the model predicted a system that uses only SHS to store energy from the compressed air will have a round-trip efficiency of 73.2% after a storage time of 24 hours, while using MgCO₃ TCES in addition to the SHS yielded a round-trip efficiency of 73.4%. The high round-trip efficiency for both cases may be caused by several assumptions made when forming the model. One of the most impactful assumptions was that an average temperature of compressed air entering the TCES reactor from the SHS could be used to perform an approximation of the discharging energy balance and therefore the amount of power generated by the turbine. The most notable consequence of this is the model not considering the lower efficiency associated with generating power from a fluid with a lower temperature. The result of this assumption is the high round trip efficiencies observed in model results. Although actual round trip
efficiencies for A-CAES systems are likely to be lower than the values predicted by the model, a comparison between the use of solely SHS and a mix of TCES SHS can be made using the model. Another major assumption was inside the reactor the TCES material and compressed air can reach thermal equilibrium. This was done because a reactor design to contain the solid MgCO₃/MgO, allow indirect heat transfer with the air, and allow released CO₂ to be captured has not been fully conceived. Consequently, the model predicts an optimistic round-trip efficiency for the TCES storage process.

The sensitivity analysis was performed, yielding the most important parameters for ensuring the implementation of TCES is more efficient than solely using SHS in an A-CAES system. The parameter that impacted the round-trip efficiency of the TCES system the most was the fraction of the total MgCO₃ in the TCES reactor that reacted during the energy storage process. The reasoning behind this is any energy that is transferred to TCES material that does not react is not recovered by the air during discharge. Reactor design is particularly crucial in ensuring the MgCO₃ can fully react.

Notably, the parameter that had the second greatest impact on round-trip efficiency was the duration of the storage. With longer energy storage times, both the purely SHS and TCES hybrid systems lose overall efficiency, but a system with only SHS loses efficiency much faster over time. Following the sensitivity analysis, the model was used to predict the round trip efficiencies for idle times varying from 1 hour to 72 hours, with the results shown in Figure 2. For idle times shorter than 14 hours, using only SHS in an A-CAES is more efficient. If energy is to be stored for a period longer than 14 hours, however, the system with TCES is more efficient. The energy stored in the chemical bonds will not be lost to the system surroundings, unlike what happens when using SHS. Improving insulation can help to mitigate heat loss but using TCES will always be better for long storage periods.

![Figure 2](image_url)

**Figure 2.** A-CAES round-trip efficiency with increased idle time for a system using only SHS and a system using both MgCO₃ TCES and SHS. Data from the model of an A-CAES system using only SHS is represented by the gray dashed line and square points, while data from the model of an A-CAES system containing MgCO₃ TCES and SHS is represented by the black line and circular points. Over long storage periods, greater than 14 hours, TCES improves storage efficiency.
The same advantage of the TCES system is observed from adjusting the SHS wall overall heat transfer coefficient, as shown in Figure 3. A higher overall heat transfer coefficient corresponds to the SHS being less insulated, allowing more energy to be lost to the surrounding environment. As the overall heat transfer coefficient increases, the round-trip efficiency of the TCES system decreases less than that of the system only using SHS. Adjusting the diameter of the SHS packed bed also had an effect on the amount of heat lost during operation, due to the relationship between the diameter of the packed bed and its surface area. A greater SHS packed bed diameter corresponded to the TCES system being favorable over just SHS.

![Figure 3. A-CAES round-trip efficiency against SHS wall overall heat transfer coefficient for a system using only SHS and a system using both MgCO\(_3\) TCES and SHS. Data from the model of an A-CAES system using only SHS is represented by the grey dashed line and square points, while data from the model of an A-CAES system containing MgCO\(_3\) TCES and SHS is represented by the black line and circular points. Over long storage periods, greater than 14 hours, TCES improves storage efficiency.](image)

The impact of charging time, which also increases the total amount of compressed air stored by the system, is illustrated in Figure 4, with charging times ranging from one to ten hours. For both systems, the round-trip efficiency increases sharply with lower charging period increases, as the SHS heats up with more air passing through it. After around six hours of charging time, the curve representing the round-trip efficiency with increasing charge time begins to flatten out, meaning increases in charge time increase the round-trip efficiency less. Additionally, the efficiency of an SHS system and a system with both TCES and SHS converge to near the same values as charge time increases. For short charge times, less than six hours, an A-CAES system using only SHS is more efficient. In a real system integrated with TCES, this is likely to be true for the additional reason that the TCES material takes time to fully react. Having the reactor temperature well above the turning temperature of the reaction will decrease the amount of time necessary for all the TCES material to react, but experimentation is necessary to ensure conditions yield the anticipated results. If the
reactor temperature is raised too high, the TCES material may experience issues such as sintering, therefore inhibiting the ability of the TCES material to react as expected.

Figure 4. A-CAES round-trip efficiency with increased charging time for a system using only SHS and a system using both MgCO₃ TCES and SHS. Data from the model of an A-CAES system using only SHS is represented by the grey dashed line and square points, while data from the model of an A-CAES system containing MgCO₃ TCES and SHS is represented by the black line and circular points. As the CAES system charges for longer periods of time, the system approaches its maximum energy storage capacity and round trip energy storage efficiency is increased.

Increasing the maximum storage pressure of the compressed air, increases the temperature of the compressed air following polytropic compression. The impact of adjusting storage pressure on round-trip efficiency is shown in Figure 5. As storage pressure and air temperature leaving the compressor increase, the energy that can be transferred to the TCES material increases. Relatively speaking, the impact of increasing storage pressure on round-trip efficiency is low and insignificant compared to many of the other parameters investigated.

Figure 5. A-CAES round-trip efficiency with increased storage pressure for a system using only SHS and a system using both MgCO₃ TCES and SHS. Data from the model of an A-CAES system using only SHS is represented by the grey dashed line and square points, while data from the model of an A-CAES system containing MgCO₃ TCES and SHS is represented by the black line and circular points. The jagged
shape of the SHS and TCES curve on the high end of pressures is seen due to low resolution caused by rounding of values at the small scale of efficiency changes observed.

4. Conclusion

To meet requirements for renewable energy integration and mitigation of intermittency in the power utility sector, the advancement of energy storage systems is necessary. Using energy from renewable sources to power CAES systems provides a solution with many notable advantages, including a long lifetime and economic competitiveness, which make it appealing for future development\textsuperscript{3,4}. The advantages associated with TCES, including high energy density and no heat loss, make its implementation into an A-CAES system worth investigating to overcome the challenges of long-term energy storage using SHS. The MgCO\textsubscript{3}/MgO reaction exhibits many qualities that are desirable for implementation into an A-CAES system that uses indirect heat transfer to store energy in TCES, including a medium turning temperature, easily separable products and an adequate enthalpy of reaction.

By modeling the implementation of MgCO\textsubscript{3}/MgO TCES in an A-CAES system and comparing its efficiency to a system that uses only SHS, the advantages of TCES were demonstrated. For energy storage periods of longer than 14 hours and for less insulated SHS, the system using TCES yielded a higher round-trip efficiency than the system using only SHS to supplement CAES. Additionally, storage at higher pressures yielded a higher round-trip efficiency for the TCES system compared to only SHS due to the increased temperature of the compressed air through the system, allowing more TCES material to react and overcome heat loss from the SHS. In all cases, it is important to note the overall loss in round-trip efficiency associated with the conditions that favored TCES implementation. If the system is to be used as modeled, the system must be intended to store energy for long periods of time, likely a day or more rather than a few hours. For short storage periods where SHS can be well-insulated, the costs of using TCES will likely outweigh any benefits.

Further research into identifying suitable TCES reactions for implementation in CAES systems should occur for both direct and indirect heat transfer schemes. To allow for more sophisticated modeling and energy analyses to be employed once more suitable TCES reactions have been identified or if research with MgCO\textsubscript{3} is to continue, a reactor allowing for indirect heat transfer to the TCES material in an A-CAES system should be designed. More comprehensive energy and exergy analyses should be completed. The use of chemical dopants and the adjustment of reactor operating conditions to ensure long-term TCES cyclability and high process efficiency need to be considered.
References


