

sCO₂ Power Cycles with Integrated Thermochemical Energy Storage Using an MgO-Based sCO₂ Sorbent in Direct Contact with Working Fluid for Grid Energy Storage Applications

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ABSTRACT

With the increasing deployment of solar photovoltaic (PV) power, advanced energy storage technology is needed to balance the electrical power supply and demand curves, especially during evening hours where PV power output is dropping rapidly, but demand is increasing. This work describes a novel thermochemical energy storage (TCES) technology, and its integration with state-of-the-art supercritical carbon dioxide (sCO₂) power cycles for concentrating solar power (CSP), waste heat, and grid energy storage applications. Current grid-scale energy storage mainly takes the form of fluid reservoir storage (pumped hydropower or compressed air, both of which are geographically limited), and electrochemical battery storage. For the first time an MgO-based CO₂ sorbent is considered for TCES applications, utilizing the reversible oxide-carbonate reaction to store and release thermal energy:



A key advantage of thermochemical energy storage systems is the small temperature range (ΔT) over which the charge and discharge cycle occurs, typically around 25-50°C. This small temperature range allows for high exergetic round-trip efficiency, and has the potential to couple well with power cycles that approximate the Carnot ideal of heat transfer at constant temperature. The solid-phase MgO and MgCO₃ reactants are contained as a packed bed reactor within a single pressure vessel. In the discharged state, the reactor is filled with MgCO₃ at a reduced temperature (650°C). To charge the reactor, CO₂ is heated in the CSP receiver up to 720°C, and a portion passes through the reactor, which decomposes the MgCO₃ to MgO and excess CO₂ or “reactive CO₂”. During energy discharge, the CSP receiver is bypassed, allowing lower temperature (470-610°C) sCO₂ to enter the reactor. A portion of this CO₂ reacts with the MgO, and releases heat, which increases the temperature of the remainder of the CO₂, which then is expanded through the power turbine in the sCO₂ power cycle. The reactant CO₂ is stored as a relatively dense fluid near its critical point when the system is in the charged state. A techno economic model is used to determine system configurations with the potential to deliver highly-efficient, low-cost energy storage (5-15 \$/kWh_{th}) on a utility scale. Preliminary results of capacity and durability of novel MgO-based sorbent are reported.

INTRODUCTION

As the installed costs of solar photovoltaic (PV) power have decreased, the increased penetration of this intermittent power source is already creating significant challenges in managing the power grid in California [1,2]. The large amount of PV power placed onto the grid during peak solar insolation periods must then be replaced by power generated through dispatchable assets in the evening hours, as the PV contribution falls off. The magnitude and distribution of this problem will continue to intensify as solar PV continues to penetrate the US power generation market.

Today, dispatchable assets that can quickly ramp generated power are primarily natural gas turbine combined cycle power plants. However, the fuel consumption and emissions from these plants negatively impact the environmental and economic advantages of renewable resources. A more favorable approach to managing the power demand requirements is energy storage. Electrochemical (battery) storage is not commercially viable at grid scales, and faces an uncertain technical and economic future. Current grid-scale energy storage mainly takes the form of fluid reservoir storage (pumped hydropower or compressed air energy, both of which are geographically limited), and thermal energy storage.

Thermal energy storage has numerous advantages over other energy storage technologies. It integrates

well with concentrating solar power (CSP), does not require specialized geographical features, and early versions are in commercial use today. The current state-of-the-art in thermal energy storage is sensible heat in the form of a hot fluid—either heat transfer oil or molten salt. The thermal stability of these heat transfer fluids limits their temperature to $< 300 / 565^{\circ}\text{C}$ respectively. These temperatures are well below those required to achieve the SunShot power block thermal efficiency target of 50% (typically considered to be $700\text{-}720^{\circ}\text{C}$ with an sCO_2 power cycle).

Other technologies (chloride- and carbonate- based molten salts, falling particle, phase-change) are considered within the EERE CSP Gen3 technology development roadmap [3], but each has numerous challenges. Among these are included high costs, complexity, and for some, highly-corrosive fluids that drive storage tank costs even higher.

The EERE CSP Gen3 roadmap [3] uses sCO_2 as the power cycle around which the storage technologies are defined. sCO_2 can integrate well with TCES due to the narrow temperature range (ΔT) over which the cycle heat addition operates. In fact, the narrow ΔT range of the MgO/MgCO_3 system allows for implementation of reheat sCO_2 cycles, which are often ignored for CSP applications due to the inverse relationship between ΔT and latent heat storage system size and cost. A single stage of reheat increases the net cycle efficiency of the sCO_2 cycle by approximately 2 points. This allows the 50% SunShot cycle efficiency target to be achieved at lower turbine inlet temperatures, which reduces the reliance upon large quantities of high-cost nickel-based alloys for the power block, thus reducing its projected cost significantly. These cycle modification studies will be conducted early in this program.

Although TCES is at an earlier stage of technology development, it has the potential for a lower-cost yet high-efficiency solution due to the physical simplicity of the integrated system, where the sCO_2 working fluid forms part of the thermochemical process.

RESULTS AND DISCUSSION

The overall goal of this project is to design, build and demonstrate a laboratory-scale, early-stage functional prototype of the MgO TCES system. In a parallel effort, a full-scale (100 MWe) system will be designed at a conceptual level. This design will encompass all the power cycle and TCES components, and will form the basis for a full techno-economic analysis (TEA) of the system. This analysis will be informed and modified by learnings derived during the bench- and laboratory-scale development work. Ultimately, the TEA will be compared against the relevant SunShot goals, including TES round-trip exergetic efficiency ($> 95\%$) and capital cost ($\$15/\text{kWh}$), and power block performance and cost (50% thermal efficiency, $< \$900/\text{kW}$ installed cost). Other areas of evaluation will include system power ramp rate and reliability.

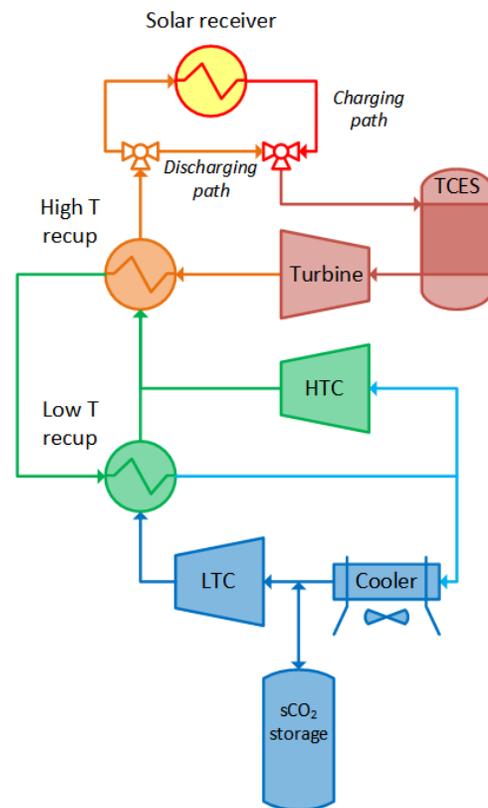


Figure 1. Unique components to the integrated sCO_2 power cycle + TCES system are the direct contact reactor and the sCO_2 storage vessels. This system makes use of all the existing sCO_2 equipment for low cost.

Technical Description

Figure 1 illustrates a simplified sCO₂ power block with the addition of two components that give it TCES capability 1) the reactor vessel and 2) the sCO₂ storage vessel. The CO₂ partial pressure equilibrium curve for MgO/MgCO₃ is given in Figure 2—the enthalpy of reaction is 108 kJ/molCO₂. Since the reaction takes place between gas and solid phases, with reasonably fast kinetics, it can be driven by a mild temperature/pressure swing to completion with high exergetic efficiency. The TCES system alternates daily between 1) the “charged state” where the reactant CO₂ is stored as a dense fluid near the critical point (30-100°C, 70-100 atm), with the sorbent decarbonated as MgO and 2) the “discharged state” where reactant CO₂ is absorbed as solid carbonate (MgCO₃) at relatively high temperature and pressure (640-670°C, 200-300 atm). During the day, the reactor pressure is maintained at 247 atm, and sCO₂, heated by the solar receiver to 720°C, enters the reactor, transfers heat to the sorbent which releases an additional 2.5-10% of sCO₂ into the flow.

The packed bed reactor has excellent heat transfer characteristics, so the outgoing fluid closely approaches the equilibrium temperature of 660°C. The sCO₂ is expanded and cooled through the normal set of expanders and recuperators and finally after the condenser the same fraction (2.5-10%) of the CO₂ reactant that was released is directed into the sCO₂ storage vessel. The process continues until the system is fully charged and the sCO₂ storage vessel is near the critical point at 72 atm and 31°C. During the nighttime cycle, the sCO₂ vessel is discharged by gradually raising its temperature to a fully discharged state of 100°C, which allows 79% of the vessel volume to be utilized. Upon leaving the sCO₂ storage vessel, the additional CO₂ mixes with the normal stream of the working fluid, is pressured up to a maximum of 300 atm, reacts with the MgO to form MgCO₃ and releases heat up to a temperature of 670°C.

The key technical challenges are the long-term CO₂ capacity performance of the MgO sorbent, the economic design of the reactor and sCO₂ vessels, and integration of the thermochemical energy storage system into the sCO₂ power cycle.

MgO Sorbent Development: An MgO-based synthetic sorbent is chosen because the thermodynamics are a good fit to the sCO₂ power cycle conditions. The raw material cost of the sorbent is very low (~150 \$/ton) and the total cost after processing has been estimated at 500 \$/ton. Southern Research has demonstrated a stable weight gain of 25% for a promoted MgO-based sorbent at 350°C (Figure 3a), and a stable weight gain of 38% for a CaO-based sorbent at 750°C (Figure 3b).

Chemically, the CaO and MgO material systems are very similar regarding the CO₂ absorption and

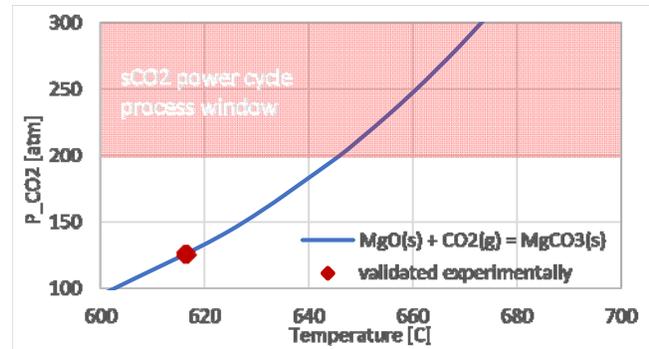


Figure 2: Equilibrium CO₂ partial pressure of the decomposition reaction with the sCO₂ power cycle. process window indicated. MgO is the sorbent of choice based on the equilibrium curve and cost. Source: Factsage web.

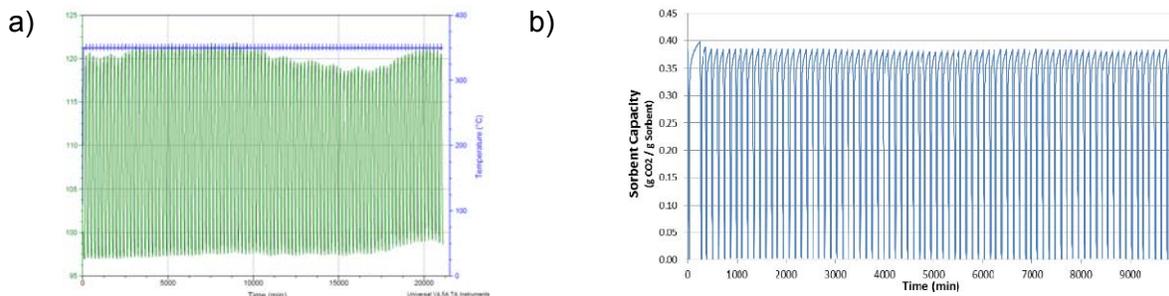


Figure 3: (Left) MgO-based sorbent exhibits a stable 25% weight gain over 150 cycles at 350°C (right) CaO-based exhibits a stable 38% weight gain over 100 cycles at 750°C sorbent. Both materials developed by Southern Research.

desorption processes. Testing MgO in the lab under these extreme conditions is challenging because no standard equipment exists. As a proof of concept to de-risk the sorbent development task SR built a 1st generation sorbent testing system loaded with a new MgO-based sorbent. The experimental system consists of a hot pressure vessel (24 ml capacity) loaded with 16 g of sorbent (800x the typical sample size of the TGA at 20 mg) connected by a 1 m long capillary tube to a cold pressure vessel (46 ml capacity) kept in a cold bath; the system is closed. The cold vessel is charged with 45 g of liquid CO₂ at 47 atm and -15 °C and then the temperature of the cold bath is increased to reach the target system pressure. By measuring the system pressure—which is uniform—and the temperature of each vessel then the total mass of CO₂ fluid is known at all times. As the temperature of the hot vessel is cycled the sorbent absorbs and releases CO₂ which is measured as a pressure rise and fall in the system and the weight capacity is calculated. Leaks are compensated for by slowly raising the cold vessel temperature to maintain system pressure, once the cold vessel reaches 60°C then the system must be recharged—a two-hour procedure, during which the hot vessel remains at target temperature. A sorbent was synthesized with the same final molar mass ratios of elements as the CaO sorbent, but Mg substituted for Ca, and with the same Mg-containing precursors used to achieve high surface area in SR's low temperature MgO-based sorbent. No promoter was added. As a screening before testing the sorbent was held in a furnace at 650°C in air (decarbonated state) and the surface area was measured at times 16, 32, and 80 hr to be 49.86, 49.76 and 50.36 m²/g, respectively. The surface area is stable at an astonishing 10x the magnitude of the CaO sorbent which itself has recently demonstrated no long-term degradation under 600 accelerated cycles in the TGA. The stability is not unexpected because the melting temperature of MgO is 239°C higher than CaO which results in a lower homologous temperature $T_H = T/T_{Melt}$, and overall less mass diffusion and sintering. The tap density was measured to be kg/m³. The system was commissioned and the experiment ran for 2 days. Leaks at the high temperature seals limited the time between recharges to ~8 hrs. The system design, instrumentation, operation and sensitivity of the analysis method were all proven successful. A Gen 2 design is already in the works which will eliminate high pressure seals and allow run times on the order of weeks. The sorbent performance can be summarized by a single observed decarbonation half cycle beginning at 126 atm and 615.8°C. The sorbent released 4.31 g of CO₂ over 29.5 min which equates to a CO₂ weight gain of 26.9%, this is a lower bound estimate, if the simultaneous system leak rate was accounted for this mass of CO₂ released would be higher.

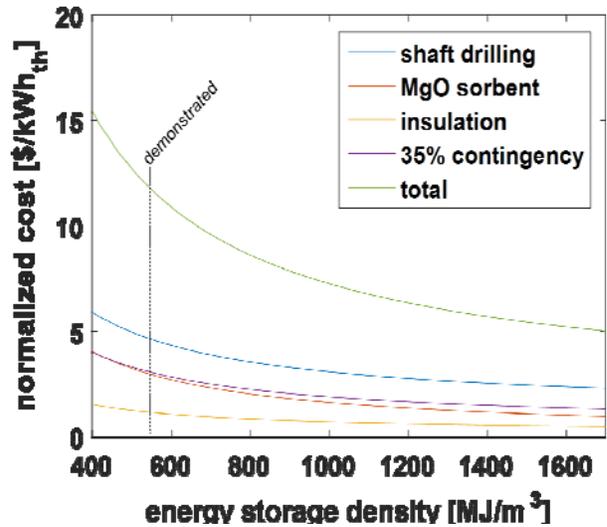


Figure 4. Itemized cost versus energy storage density of the material. Assuming a d=16 [m] shaft diameter. Major cost drivers are the sorbent storage density cost of underground storage i.e. shaft drilling

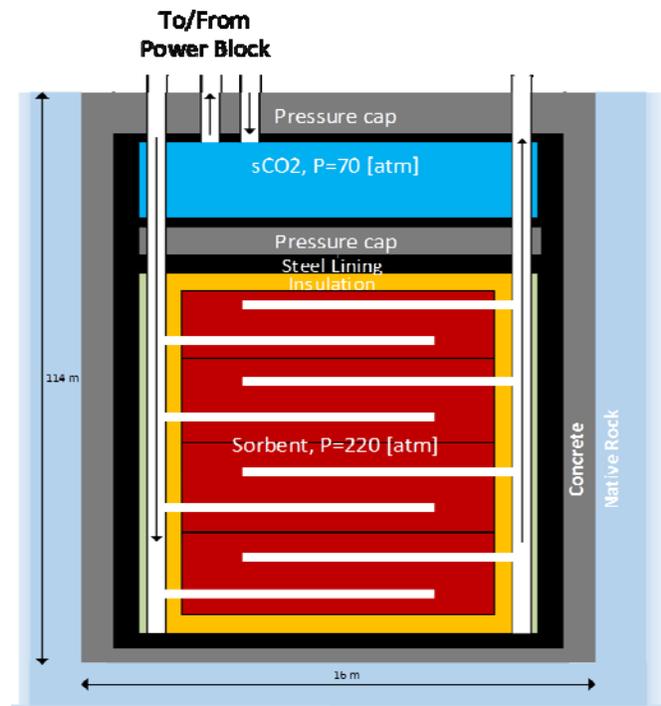


Figure 5. Underground reactor and sCO₂ storage vessels. A single shaft up to 16 m dia, 114 m deep with 200-300 atm in the reactor vessel and 70-100 atm in the sCO₂ storage vessel.

The following conclusions can be drawn, 1) the equilibrium curve predicted by thermochemical modeling is verified (Figure 2), 2) the reaction kinetics are fast enough that a promoter may not be necessary 3) the overall energy capacity equates to 547 MJ/m³ which is within TEA targets (Figure 4), 5) the low-cost manufacturing method is suitable for this application. Although the long-term durability of the sorbent has not been characterized there are still many parameters to optimize for increased performance, including the addition of promoters.

Underground reactor and sCO₂ storage vessels

Conventional steel vessels for thermal storage applications can be cost-prohibitive due to the large volumes of fluid required for the reactions, even at the high density of sCO₂. A preliminary survey of subterranean gas storage has turned up two potential options: 1) salt cavern storage at a cost of 5-50 \$/m³ provides an inexpensive storage technology, however, it is limited to very specific geological sites [5,6]. 2) Large-diameter drilled shafts at a cost of 400 \$/m³ remove the geological constraints, as the shafts can be drilled into most rock formations, which are then lined and sealed using cement [6]. The drilled shaft design assumed for the TEA that follows, requires much less material for construction than above-ground systems because the surrounding earth acts as a nearly infinite wall thickness and can withstand internal pressure >80 MPa. The sorbent reactor is up to 114 m tall and is divided into several stages of packed beds, operated in parallel and optimized for low pressure drop and structural support (Figure 5). Particle/pellet size and crush strength of the sorbent are important parameters that dictate the design. Low pumping power is easy to accomplish in the large packed bed reactor assuming a path length of 5 m (height of each packed bed stage) then particle sizes of 200 and 650 μm would produce a pressure drop of 1 and 0.1 atm; larger pellets of several mm are commonly manufactured and would further decrease the pressure drop. The reactor is lined with a 2 meter thick layer of insulation which could be composed of waste powder from the sorbent manufacturing process, outside of that is a thin layer of sCO₂ cooling fluid—also at an equal pressure of the reactor—to limit the temperature of the shaft walls. The sCO₂ storage is 25 m tall and is located above the reactor with a single inlet and outlet. Figure 4 plots the normalized individual and total costs of the system versus the reactor energy storage density. Based on results of preliminary sorbent characterization the total projected total cost is \$11.8 kWh_{th}. The theoretical energy density of pure MgO sorbent is 3773 MJ/m³, however there are several practical considerations that will reduce the energy density of the reactor itself. A packed bed of particles/pellets will have a void fraction of 0.26 which is needed to allow mass and heat transfer through the bed. To avoid pore plugging it needs an excess void fraction of 0.038 in the carbonated state and a volume fraction of 0.075 of inert solids to stabilize the MgO and a volume fraction of 0.075 of promoters to increase kinetics. This leaves 0.56 volume fraction for MgO+MgCO₃ in the carbonated state. Assuming an extent of reaction of 60% (conversion from MgO to MgCO₃) then the highly engineered packed bed reactor would have an energy density of 1700 MJ/m³, we use this value as the practical upper limit in the TEA, while we only need to actually achieve a minimum value of 410 MJ/m³ to hit cost targets.

Energy, exergy analysis

The size of the reactor corresponding to the 15 \$/kWh_{th} scale (worst case in Figure 4) is a D=14 m and a height of 114 m and insulated all around with 2 m of insulation. Assuming a temperature difference of 600°C and that none of the heat can be recovered (worst case) the thermal conductivity required to achieve ≤ 1% heat loss is ≤0.5 W/mK which is achievable with powders. The round-trip exergy efficiency was calculated by considering the exergy transfers across a control volume enclosing the reactor from the following sources: 1) sensible heat as sCO₂ working fluid 2) chemical exergy as sCO₂ reactant 3) mechanical work as pumping power 4) heat loss via conduction. Reactant CO₂ outside the reactor volume is considered part of the power cycle efficiency since it follows an identical path as the working fluid. Managing flow rates and controls will in general affect the power cycle efficiency however this is considered a secondary effect and was neglected in the analysis. Assume the round-trip thermal efficiency is 99% and during charging sCO₂ enters the reactor at 720°C and exits at 660°C. If during discharge the sCO₂ enters at 610°C and exits at 660°C then the round-trip exergy efficiency is 96.1%.

Reliability, risk

The drilled shafted vessel provides a reliable solution that is protected from harsh weather and

unforeseen human events on the surface. The sorbent material is tolerant to temperature excursions and can be cooled to room temperature without negative consequences. The large porosity allows the bed to accommodate thermal expansion more so than a latent heat system. Potentially the sorbent can even be replaced, for instance by cooling to room temperature and then pumping liquid CO₂ or liquid water in the reverse direction to fluidize the bed and pump the sorbent out.

The sorbent contains no volatiles compounds based on thermochemical modeling. The sCO₂ turbomachinery is known to be tolerant of particles <30 μm at small concentrations which tend to move with the flow and not impinge on the blades. Several strategies will be invested to mitigate damage by solid sorbent entrained in the flow including: optimization of fluid velocity and direction to avoid fluidization of the bed, filters, cyclone filters, a binder added to sorbent to minimize the generation of fines.

Conclusions

A novel TCES system was described in which heat is stored in a reversible thermochemical carbonation/decarbonation reaction with MgO/MgCO₃ at high pressure and temperatures from 570-685 °C. The system is highly efficient with a round-trip exergy efficiency of 96% and low cost with a path to installed costs <10 \$/kWh_{th}.

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Dr. Andrew Muto is a Senior Engineer with over 10 years' experience in development of advanced energy conversion and storage systems, advanced thermal systems, process development and several leadership roles. He has served as co-PI on two SunShot sponsored technology development projects under the ELEMENTS and APOLLO programs in development of large scale thermochemical energy storage (TCES). He is technical lead on a third SunShot project for MgO-based TCES under the Tech to Market program where SR is a sub-prime partner to Echogen. He has a PhD in Mechanical Engineering from MIT.