APOLLO Phase 2 – Final Technical Report (Public)

Project Title:	Demonstration of High-Temperature Calcium-Based Thermochemical Energy Storage System for use with Concentrating Solar Power Facilities
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Executive Summary

Thermochemical energy storage (TCES) systems offer several advantages over sensible heat storage via molten salts for concentrating solar power (CSP) including: energy density, cost, indefinite storage time, and no risk of freezing. SR's TCES system utilizes a CaO-based carbonation reaction at high temperature in a fixed bed heat exchanger reactor. The SunShot APOLLO project focuses on the validation of the calcium oxide sorbent for capacity, durability, system economics, and demonstration of the system at a small pilot scale, including system control and operation in simulated on-sun conditions, discharging at 720ºC.
Under phase I SR completed evaluation of the sorbent loaded in a single-channel heat exchanger reactor. The major accomplishments of phase II are:

- Design, fabrication and commissioning of a 4 kWh_{th} pilot plant (50x capacity increase from previous bench scale) with a closed-loop CO_2 system, and a commercially relevant heat exchange reactor. The heat exchange reactor has been designed with state-of-the-art modeling tools to ensure 1) sufficient lifetime of the Incoloy body and 2) performance of the packed bed reactor will be adequate to meet the milestones. The rest of the pilot system has been designed with off-the shelf components to maximize reliability and cost effectiveness. The system is highly instrumented and capable of time resolved, independent measurements of the heat and mass balances respectively.
- Major developments in the technoeconomic analysis (TEA) include 1) reduction of the cost of membrane gas storage for the near-term and future systems and 2) integration with liquid metal receivers and particle receivers for higher decarbonation temperatures and pressures which reduced the cost of gas compression and increased system efficiency. The result are three scenarios with costs bases of $21.9, $14.3, and $10.9/$kWh_{th}$ corresponding to a real LCOE of 59, 57, 56 $/$MWh_e$, respectively.
- The basic operations of the energy storage system were demonstrated for carbonation (discharging) and decarbonation (charging) over short time periods. Excellent control of the CO_2 mass balance across the reactor was achieved with mass flow controllers and the basic operation of the level control of the CO_2 gas bladder was achieved. The system was apparently free from leaks and operated continuously for 18 days with no mechanical failures, thus meeting milestone 2.5.5. The major shortcomings of the system had to do with the controls which prevented us from deep cycling and or reaching high cycles. We were unable to decarbonate (charge) the system for more than a few minutes at a time, which was much shorter than the design target of 10 hrs. This issue could not be resolved due to facility availability and contract closure.

One major finding is that CaO-based TCES is most cost efficient when charged with HTF (heat transfer fluid) temperatures >850ºC to reach the round-trip exergy efficiency and system cost targets which are higher temperatures than those considered for Gen 3 CSP. Many of the balance of plant components do not exist today, however we are encouraged by our findings that in general with more work we are able to reduce the capital cost, for example with the membrane gas storage, which is an innovative component in itself. The CaO-based TCES system has potential to meet the latest SunShot 2030 goals of LCOE at 50 $/$MWh_e$ with capital costs of <11/kWh_{th}.

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Introduction & Project Objectives

The objective of this project is to demonstrate a high-temperature calcium-based thermochemical energy storage (TCES) system for use with concentrated solar power (CSP) facilities. The project will culminate in the demonstration and evaluation of a 4 kWh_{th} system to be discharged at 720ºC under simulated on-sun conditions. The engineered calcium-based sorbent developed by the project team under the ELEMENTS program has successfully shown stable and high capacity performance in accelerated laboratory scale testing. Sorbent needs to be produced in sufficient quantity for use in the 4 kWh_{th} system (pilot system), and the performance of this large batch needs to be validated. The pilot system will be designed, commissioned, installed, and shown that any changes do not affect the ability of the technology to meet cost and performance requirements at commercial scale. In addition, options for gas storage will be evaluated and if needed, an optimized sorbent recovery strategy will be developed and their impacts on commercial system economics assessed. Integration of the TCES system with the sCO_2 power cycle can potentially impact optimum system economics. A design optimization and integration study is needed to evaluate options for system integration that minimize impact on sCO_2 power block operation, but optimize heat integration, CO_2 use and storage, and overall system economics.

The report is organized by tasks, milestones are summarized in Table 1. The body contains a subset of tasks necessary to understand the project as a whole, the rest are contained in the appendix. The first section of the appendix "Background Literature Search" is recommended for readers not familiar with CaO-based energy storage systems.

Project Results and Discussion

Table 1 summarizes progress in terms of SOPO milestone achievement. The subsections following the milestone summary table describe the technical results of a subset of the milestones.

Table 1. Milestone Summary Table

	Metric Definition (From Measurement)	Success Value	Measured Value	Assessment Tool	Goal Met (Y/N)	Supporting Data & Notes
Summary of rationale for 1.1.X milestones: *demonstrate a high capacity, high durability sorbent which can be repeatably produced and scaled up for the prototype system*						
1.1.1	Using large batch sorbent in 50 cycle accelerated TGA testing, achieve total CO2 capacity as represented by the average mass of CO2 absorbed over the 50 cycle test divided by the mass of the fully decarbonated sorbent: $\frac{mass_{CO2\ absorbed,av}}{mass_{decarbonated\ sorbent,av}}$	> 0.38	(A) 0.406 ±0.005 (B) 0.408 ±0.005 (C) 0.410 ±0.005 Avg: 0.408 ± .0024	One-sided Student's t-test; 95% Confidence Interval (C.I.);	Y	50 cycle test of PCI 1kg large batch powder evaluated on TGA. Same test to be repeated (in triplicate) with Clariant developed sorbent. Error estimate on individual runs (A)-(C) is 95% CI using calculated instrument error. Test has been replicated for t-test assessment, shown with the Measured Value Average.
1.1.2	Using large batch sorbent in 50 cycle accelerated testing, achieve ratio of mass absorbed in final cycles to mass adsorbed in initial cycles, defined as: $\frac{average\ capacity\ cycles\ 45-50}{average\ capacity\ cycles\ 10-20}$	> 0.99	(A) 0.996 ± 0.017 (B) 0.985 ± 0.017 (C) 0.985 ± 0.017 Avg: 0.99 ± .01	One-sided Student's t-test; 95% Confidence Interval (C.I.);	Y	50 cycle test of PCI 1kg large batch powder evaluated on TGA. Same test to be repeated in triplicate with Clariant developed sorbent. Error estimate on individual runs (A)-(C) is given by $\sqrt{2}\ C/\bar{X}$, where C is the 95% Confidence interval reported in milestone 1.1.1, and $\bar{X}$ is the reported average from the same. Test has been replicated for t-test assessment, shown with the Measured Value Average.

	Metric Definition (From Measurement)	Success Value	Measured Value	Assessment Tool	Goal Met (Y/N)	Supporting Data & Notes
1.1.3	Using large batch sorbent in 25 cycle non-accelerated 0.5L bench scale testing, achieve total CO_2 capacity as represented by the average mass of CO_2 absorbed over the 25 cycle test divided by the mass of the fully decarbonated sorbent: $\frac{mass_{CO2\ absorbed,av}}{mass_{decarbonated\ sorbent,av}}$	> 0.45	0.312 ± 0.003 (see comment A) 0.278 ± 0.004 (see comment B) 0.283 ± 0.002 (see comment C)	One-sided Student's t-test; 95% C.I.	N	(A) Preliminary 12 cycle test of PCI 1kg large batch pellets evaluated in 250g bench unit on shortened 3-hr half-cycles. (B) First 25 cycles of 72 cycle test using PCI 1kg large batch pellets evaluated in 250g bench unit on 7.5 hr half-cycles. (C) 67 cycles of 72 cycle test using PCI 1kg large batch pellets evaluated in 250g bench unit on 7.5 hr half-cycles. Error estimate presented is 95% CI using experimental variance (from residuals to capacity curve fit). Empirical errors are consistent with propagated instrument error. Same test to be repeated on Clariant developed sorbent prior to end of Phase I.

	Metric Definition (From Measurement)	Success Value	Measured Value	Assessment Tool	Goal Met (Y/N)	Supporting Data & Notes
1.1.4	Using large batch sorbent in 25 cycle non-accelerated 0.5L bench scale testing, achieve ratio of mass absorbed in final cycles to mass adsorbed in initial cycles in 25 cycle test, defined as: $\frac{average\ capacity\ cycles\ 20-25}{average\ capacity\ cycles\ 6-19}$	> 0.99	(A) 0.923 ±0.17 (B) 1.034 ± 0.015 (C) 0.972 ± 0.015	One-sided Student's t-test; 95% C.I.	Y (large-batch sorbent in 67-cycle test and formula specified in milestone) N (other test and calculation methods)	(A) Preliminary 12 cycle test of PCI 1kg large batch pellets evaluated in 250g bench unit on shortened 3-hr half-cycles. (B) Durability of 67 cycle test as strictly defined by milestone 1.1.4 (C) Durability of 67 cycles using cycles 16-52, and 53-67 Error estimate on individual runs (A)-(C) is given by $\sqrt{2}\ C/\bar{X}$, where C is the corresponding 95% Confidence interval reported in milestone 1.1.3, and $\bar{X}$ is the reported average from the same. Testing will be completed using new sorbent in remainder of Phase I period.
Summary of rationale for 1.2.1 - 1.3.2 milestones: *How resilient is the sorbent? If there is a process upset such as temperature excusions or held in decarbonated state for a long time will the sorbent recovery back to previous capacity? Note that is was later found that control of the temperature is quite is since it operates close to equilibrium at all times (see appendix"* Constant slope experiments*")*						
1.2.1	Ratio of mass absorbed in 5 cycles after sorbent recovery to mass adsorbed in 5 cycles before intentional 10% sorbent degradation	> 0.99	0.998 ± 0.00004 (Powder) 0.995 ± 0.00004 (Pellet)	One-sided Student's t-test; 95% C.I.	Y (Powder and pellets – 1st1st of 3 planned replicates)	Results provided are for a single full recovery test. Two replicates are in progress. Error estimate is 95% CI for single tail t-distribution, with n=3 (df=2), where sigma is determined from propagated instrument error.

	Metric Definition (From Measurement)	Success Value	Measured Value	Assessment Tool	Goal Met (Y/N)	Supporting Data & Notes
1.3.1	Peak temperature difference along flow axis between HTF and sorbent material: $T_{max,tube} - T_{min,sorbent}$ (Charging) $T_{max,sorbent} - T_{min,tube}$ (Discharging);	< 25C	<16°C from experimental reactor; Modeling Complete: $T_{max} = T_{eq}(P_{CO_2})$	Probabilistic Analysis, via Monte Carlo simulation, to determine the range of temperature difference and associated probability distribution based on variance of cycle time, transient heat transfer rate, and HTF inlet temperature	Y	• Temperature differential measured experimentally meets criteria on bench scale reactor. • Model development of commercial reactor underway and will confirm proper dT for optimized reactor design. • Monte Carlo not appropriate assessment tool. Parametric evaluation preferred.
1.3.2	Bi-directional exergetic efficiency of the full energy storage system: $\frac{EX_{Q,HTF-OUT} + EX_{W,COMP-OUT}}{EX_{Q,HTF-IN} + EX_{W,COMP-IN}}$	> 95%	Constant slope results show 98.0% ± 0.1% exergetic efficiency Model indicates >96-98.8%	Probabilistic Analysis via Monte Carlo simulation, demonstrating that >95% of the probability distribution meets the success value based on variance of cycle time, transient heat transfer rate, and HTF inlet temperature	Y	• Exergetic efficiency measured experimentally meets criteria in TGA constant slope experiment. • Model of commercial reactor confirms exergetic efficiency of the reactor and HTF >98% for all foreseeable designs • Monte Carlo not appropriate assessment tool. Parametric evaluation

Summary of rationale for 1.3.3, 1.3.4 milestones: *Assure that chosen recipe which meets performance targets above also simultaneously meets technoeconomic targets.*

	Metric Definition (From Measurement)	Success Value	Measured Value	Assessment Tool	Goal Met (Y/N)	Supporting Data & Notes
1.3.3	Calculated specific capital cost of sorbent loading procedure and material at commercial scale (~2 GWh). Does include cost of sorbent itself: $\frac{\$\ Capital\ Cost}{kWhr_{thermal}}$	< 3.0	$2.56 +/-$0.44 (85% cases meet criteria) 95% threshold is $3.36	Probabilistic Analysis via Monte Carlo simulation, demonstrating that >95% of the probability distribution meets the success value based on variance of sorbent packing density, void fraction, and HX channel width	N	Capital Costing and Probabilistic Analysis tools developed and preliminary simulations run (30,000 MC runs), showing ability to meet success criteria for >95% of cases for certain assumed sorbent capacity (0.25-.45), cost ($500/ton), and lifetime (9-25 years), all of which are more important than effects of density, void fraction, and channel width. See Exhibit B. Clariant has confirmed initial estimates of $500/ton are feasible, but cannot finalize a price until a full TEA is completed.
1.3.4	Calculated specific capital cost of commercial scale (~2 GWh) full energy storage system (heat exchanger reactor, compressor, gas storage, and BOP). Does not include cost of sorbent or sorbent loading: $\frac{\$\ Capital\ Cost}{kWhr_{thermal}}$	< 12.0	$39.66 +2.46/-3.03 (No Designs Meet Criteria)	Probabilistic Analysis via Monte Carlo simulation demonstrating that >95% of the probability distribution meets the success value based on variance of cycle time, transient heat transfer rate, and HTF inlet temperature	N	Capital Costing model (ASPEN and additional tools) and Probabilistic Analysis tools (Monte Carlo) are completed. Additional data from equipment manufacturers and vendors has been collected and incorporated into completed costing runs.

Summary of rationale for 1.3.5 milestone: *Energy storage solutions must have the ability to throttle output based changing solar input due to passing clouds and other transients. Demonstrate the ability to control the overall heat transfer rate.*

	Metric Definition (From Measurement)	Success Value	Measured Value	Assessment Tool	Goal Met (Y/N)	Supporting Data & Notes
1.3.5	In the ~0.5L bench scale system, achieve and maintain (within 2.5%) reversible steady state heat transfer rates of 50, 100, and 250 kW_{th} throughout full range of operating CO2 partial pressures of 0.01 – 0.20 bar in an isothermal system (>720°C) for 2-3hrs tests	Maintainheat transfer rates of 50, 100, 250, -50, -100, -250 kW_{th}	Average 62.9 ± 11.7 $kW_{th}/Ton_{sorbent}$ during 8 hour carbonation. Heat transfer rate expected to scale with the inverse of the carbonation period, which would yield 251.6 +/- 46.8 $kW_{th}/Ton_{sorbent}$ over a 2 hour carbonation	One-sided Student's t-test; 95% C.I.	--	• Rate control testing was completed on TGA to validate control methods for steady state heat rate, prior to implementation at larger scale, to reduce risk to bench scale sorbent. Additional testing and modeling to be completed at bench scale after sub-atmospheric conversion to address milestone and remainder of task 1.3.3. • Heat rates specified in milestone are for pilot scale reactor, not bench scale. • Benchscale heat transfer rates calculated as the average of the integral of instantaneous greatest temperature difference within the HTF stream. Error estimate presented is 95% CI using experimental variance. A fitting parameter of 15 $kW_{th}/Ton_{sorbent}$ was used to account for aggregate heat losses in the system.
Summary of rationale for 1.3.6, 2.1.1 milestones: *Communicate with commercial partners early to ensure technoeconomic needs are being met and build a path to market.*						
1.3.6	Have NDAs with potential commercialization partners signed	3	10	Signed agreements	Y	Confidential
2.1.1	NDA with at least 1 sCO_2 developer	1 NDA signed	1	Copy provided to DOE (deadline Q1)	Y	**Confidential**

	Metric Definition (From Measurement)	Success Value	Measured Value	Assessment Tool	Goal Met (Y/N)	Supporting Data & Notes
Summary of rationale for 2.2.1 milestone: *Literature studies have shown the benefit of steam recovery on the labscale. As a next step prove the practicality of switching from a pure CO2 environment to a pure H2O environment and back. Note that this is not a demonstration of the overall efficacy of at Communicate with commercial partners early to ensure technoeconomic needs are being met and build a path to market.*						
2.2.1	Steam Recovery Capability and Control Demonstrate reversible steam-hydration reaction at steady state on the benchscale reactor: $CaO+H_2O=Ca(OH)_2$	≥ 5 steam charge/discharge cycles achieving a steady state Constraint: Steam recovery; Bench-scale Reactor; Standard deviation of Weight capacity ≤ 10% (~ +-4 ml of liq. H_2O)	H2O Capacity: 13.68±0.55% (7.59 mmol/g) (T = 1.771) Degradation: -3.8% per 100 Cycles (P=0.5986)	One-sided Student's t-test; 95% C.I. (deadline Q1)	Y	T-value based on number of cycles. P-value based on slope of linear fit.
Summary of rationale for 2.5.X milestones: *Testing metrics for the prototype system which will demonstrate the system has been design correctly and validates technoeconomic assumptions.*						

	Metric Definition (From Measurement)	Success Value	Measured Value	Assessment Tool	Goal Met (Y/N)	Supporting Data & Notes
2.5.1	Heat Transfer Rates Demonstrate ability of 4 kWh_{th} system to achieve steady state heat transfer rate: $MassFlow_{HTF} * (h_{HTF, out} - h,_{HTF, in})$	> 0.4 kW_{th} (10-hr avg heat release rate) Constraints: Hold constant (95% C.I. is within 2.5% of mean) for 30 minutes. ≥5 separate runs at identical target value. Note: ~13kg of sorbent[1]	incomplete	Has the heat transfer rate stabilized? two-sided Student's t-test; 95% C.I. about mean of each run Is the stabilized value repeatable over multiple cycles? one-sided Student's t-test; 95% C.I. about the mean of the means for the 5 run set	N	Refer to PFD (P&IDs available by request), Comsol modeling, contruction pictures

[1] Assuming heat of reaction is 170 kJ/mol_CO_2 = 3862 kJ/kg_CO_2, and a maximum capacity of 0.28 g_CO2/g_sorbent

	Metric Definition (From Measurement)	Success Value	Measured Value	Assessment Tool	Goal Met (Y/N)	Supporting Data & Notes
2.5.2	Heat Transfer Rates Demonstrate ability to <u>dynamically follow</u> heat transfer load profiles $MassFlow_{HTF} * (h_{HTF, out} - h,_{HTF, in})$	Discharging Within the same half-cycle: 0.4 kW_{th} (10-hr avg) 0.2 kW_{th} (20-hr avg) Charging Within the same half-cycle: -0.4 kW_{th} (10-hr avg) -0.2 kW_{th} (20-hr avg) <u>Constraints</u>: two power levels achieved within each carbonation/decarbonation half cycle. Hold constant (95% C.I. is within 2.5% of mean) for 10 minutes. ≥5 separate runs at identical target values.	incomplete	*Has the heat transfer rate stabilized?* two-sided Student's t-test; 95% C.I. about mean of each run Is the stabilized value repeatable over multiple cycles? one-sided Student's t-test; 95% C.I. about the mean of the means for the 5 run set	N	Phase I bench scale reactor demonstrated precise control of the reaction. This is an engineering challenge we expect to meet in Q4.
2.5.3	Heat Transfer Rates Demonstrate ability to meet <u>peak</u> heat transfer rates $MassFlow_{HTF} * (h_{HTF, out} - h,_{HTF, in})$	> 0.8 kW_{th} (5-hr avg heat release rate) <u>Constraints</u>: Hold constant (95% C.I. is within 2.5% of mean) for minimum of 15 minutes. ≥5 separate runs at the same target value	incomplete	Has the heat transfer rate stabilized? two-sided Student's t-test; 95% C.I. about mean of each run Is the stabilized value repeatable over multiple cycles? one-sided Student's t-test; 95% C.I. about the mean of the means for the 5 run set	N	Reactor was designed and modeling with Comsol in order to meet this milestone (Figure 17)

	Metric Definition (From Measurement)	Success Value	Measured Value	Assessment Tool	Goal Met (Y/N)	Supporting Data & Notes
2.5.4	Full Energy Capacity Validation Demonstrate full capacity by deep cycling	$4kWh_{th}$ Constraint: Full capacitive discharge profiled in time; ≥5 separate runs. Heat transfer rate ≥0.2 kW_{th} (20-hr avg) at all times	incomplete	One-sided Student's t-test; 95% C.I.	N	Reactor capacity is designed to meet milestone with a factor of safety.
2.5.5	Reliability Demonstrate continuous cycle operation for 14 days	No shut-downs, equipment failures, or controls interruptions	18 days with no mechanical failures	System is still functional Inspection Checklist, provided to DOE	Y	Expected to be met. (Benchscale was operated for ~1 year)
Summary of rationale for 2.5.6 milestone: *Self-explanatory*						
2.5.6	Tech-to-Market Complete test plan for Phase 3, with input from commercial CSP developers	DOE acceptance CSP developer acceptance and documented input.	Tech to Market Plan.docx	NA – Binary Formal Test Plan document with DOE Approval. Summary memo of CSP developer input Completed Tech2Market Template:	Y	Embedded Document
Summary of rationale for 2.6.1, 2.6.2 milestones: *Final technoeconomic evaluation of phase II, breaking up costs into sorbent and balance of plant to show a path to cost cutting which can continue with more development and to be substantially under molten salts.*						
2.6.1	Based on pilot system data, calculated specific capital cost of 30-year sorbent expenses at commercial scale (2 GWh). Does include cost of sorbent itself: $\frac{Cost\ of\ 30y\ sorbent\ managment\ plan}{kWh_{thermal}}$	< $3.0/$kWh_{th}$	10% sorbent Replacement per year, one 40-ton truck every 22 days. Replacement cost: $2.62/$kWh_{th}$	Any cases with calculated values less than $4 will then be analyzed with a Monte Carlo simulation.	Y	Assumes a residual capacity of the sorbent that is 2/3 the original

	Metric Definition (From Measurement)	Success Value	Measured Value	Assessment Tool	Goal Met (Y/N)	Supporting Data & Notes
2.6.2	Based on pilot system data, calculated specific capital cost of commercial scale (2 GWh) full energy storage system (heat exchanger reactor, compressor, gas storage, and BOP). Does not include cost of sorbent or sorbent loading: $\frac{\$\ Capital\ Cost}{kWhr_{thermal}}$	< $21.0/kWh$_{th}$	Three scenarios at $21.9/kWh$_{th}$ ($59.1/MWh$_e$), $14.3/kWh$_{th}$ ($57.1/MWh$_e$), $10.9/kWh$_{th}$ ($56.3/MWh$_e$),	Sensitivity analysis will be used to narrow the case selection criteria. Probabilistic Analysis via Monte Carlo simulation demonstrating that >68% of the probability distribution meets the success value based on variance of costs of materials and components	Y	
Summary of rationale for 2.5.6 milestone: *Self-explanatory*						
2.6.3	Identify potential licensing partner	1		Signed memorandum or Expression of Interest	N	near-term application is for process heat. DOE-Echogen project with MgO-based TCES. See milestone 2.5.6)

Task 1.3 – COMSOL and Aspen Modeling, Techno-Economic Analysis, Field System Design, Closed Loop Control, Commercial Partnerships

The commercial reactor was originally envisioned as a mixture of CO_2 and a carrier gas circulated through a packed bed, this design has become infeasible from a balance of plant perspective due to additional storage, sensible heat recovery and circulation equipment of the carrier. We have converged on a pure CO_2 system which has **higher exergetic efficiency** and more **precise control of heat output**. The circulated mixture design produced a moving heat wave in the flow direction; to accurately predict this requires accurate characterization of the transport kinetics of the sorbent (with temperature dependence) which is coupled to fluid flow—a rather complex model. With the pure CO_2 design all gas entering the reactor gets absorbed and releases heat (with a short time delay), this means that the static bed (not moving) reactor is insensitive to transport kinetics, though more sensitive to the thermal conductivity of the sorbent—ultimately it is a simpler system to characterize and control.

Subtask 1.3.1 – COMSOL Modeling of Heat Exchanger Reactor, System Modeling of Bi-directional Exergetic Efficiency, Commercial Reactor Design

Milestone 1.3.1 was experimentally demonstrated by the bench scale reactor, the measured maximum temperature difference was less than 16ºC for all runs. Originally it was thought that the highly exothermic carbonation reaction could run out of control, heat up to high temperatures and damage the sorbent. Similar to a catalyst bed with a highly exothermic reaction. We now know that under commercially relevant conditions the carbonation reaction is approximately 1st order, transport kinetics are relatively fast (compared to heat transfer) and the maximum temperature of the bed is always thermodynamically limited by the pressure of CO_2 supplied. For any commercial design, hot spots are avoided in **all cases** by limiting the difference between the equilibrium temperature of the incoming CO_2 (based on CO_2 partial pressure) and the actual average wall temperature

$$\Delta T_{\max} = T_{eq}\left(P_{CO2}\right) - \overline{T}_{wall}. \qquad \textit{Eq. 1}$$

It is an important parameter that effects the exergy efficiency and economics of the reactor. Milestone 1.3.1 specifies that $\Delta T_{\max} \leq 25^{o}C$ which is possible but not likely to be optimal based on cost of the heat transfer surface area in the reactor. The conclusion is that control of the reaction and sorbent temperature is relatively simple; rather than needing a statistical Monte Carlo method to identify unstable system states, we are stable and deterministic everywhere, the maximum theoretical sorbent temperature is known at all times. Since $\Delta T_{\max}$ is known with certainty it can be used as a sweeping parameter in a multivariable optimization of system cost and exergy efficiency (Figure 5). Milestone 1.3.1 was experimentally demonstrated in the bench scale reactor, the measured maximum temperature difference was less than 16ºC for all runs (Figure 1).

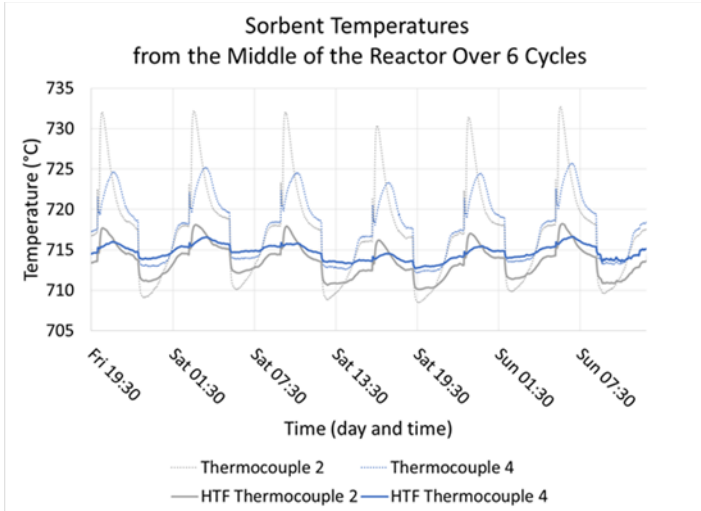


Figure 1: Temperature versus time for positions along the sorbent axis perpendicular to flow in the bench scale reactor system. Six carbonation, de-carbonation cycles are plotted.

Milestone 1.3.2 – Exergetic Efficiency

The target milestone for exergetic efficiency was established in order to meet levelized cost of electricity targets and associated energy storage costs. To evaluate the exergetic efficiency of the proposed TCES system, data from a series of experiments was evaluated to validate exergetic efficiency experimentally. Milestone 1.3.2 was experimentally demonstrated in the TGA with a value of 98.0+-0.1% for commercially relevant cycles. This demonstrates that the exergy loss from reaction kinetics alone is small.

To further evaluate the exergetic efficiency and impact of system design and operating parameters, a model of the system was developed using MATLAB, which allowed us to quickly investigate a great number of cases. The model assumes steady state operating set points therefore it applies for an arbitrary reactor design space for optimization. The bi-directional or round-trip exergy efficiency is calculated by making a control volume around the entire system and calculating the ratio of useful exergy transfers out to exergy transfers into the system, which includes transfers from the HTF, CO_2 gas and HTF dissipated pumping power. For the entire plant, the exergy efficiency calculations include the HTF transfers, HTF dissipated pumping power, compressor power, turbine power and additional heat input needed for a potential gas sensible heat storage system that can improve system efficiency by reducing heat losses.

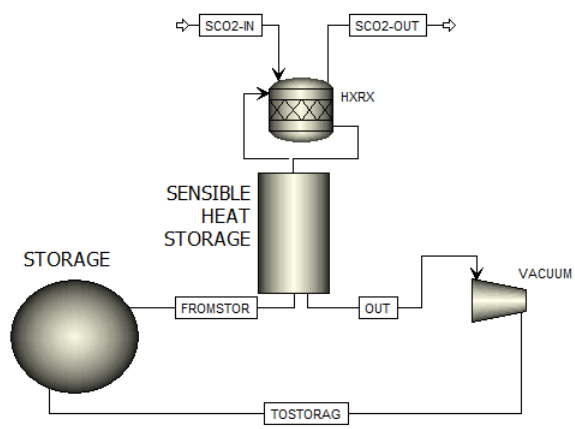


Figure 2: System process flow diagram for TCES system. It contains the HXRX, a primary sensible heat storage system, compressor, CO_2 storage, and an optional turbine (not shown).

The first system considered imposes the constraint from milestone 1.3.1, that $\Delta T_{\max} = 25[C]$. The bi-direction exergy efficiency

of the system versus T_{max} is given in Figure 3, for a variety of cases, so one can analyze where the losses are. The following cases are evaluated:

- base case solution with current technology and the least optimistic assumptions
- base case plus turbine,
- base case plus turbine and compressor with a larger polytropic efficiency of 0.80 (versus 0.30 for current technology) which is an attainable value for gases at or above 1 [atm].
- base case plus above and an ideal packed bed sensible heat storage system with negligible pressure drop and approach temperature differential.
- base case plus above plus additionally assumes the ideal, reversible adiabatic compressors and turbines.
- Above case plus ideal, reversible isothermal compressors and turbines which is the theoretical best.
- Reactor only (including pumping power of HTF)

For the reactor only case, which corresponds to milestone 1.3.2, the exergetic efficiency is very high at ≥0.987. This has also been demonstrated both in the TGA and bench scale reactor that this value is attainable over commercially relevant cycle times.
It should be noted that the 'reactor only' (blue) and 'ideal isothermal' (orange) solutions should exactly match, but they deviate by 1 percentage point. This discrepancy is mostly likely explained by disagreement between the equilibrium curve of the carbonation reaction and the ideal gas with constant specific heat as assumed for the balance of plant.

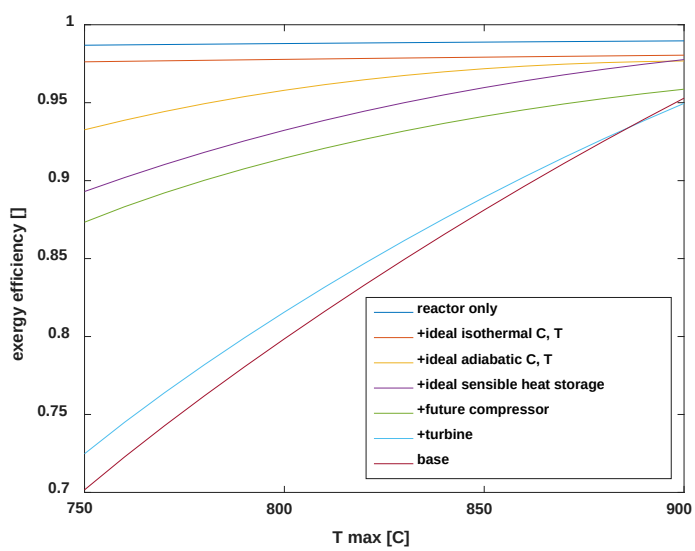


Figure 3: Bi-direction system exergy efficiency versus maximum temperature for different assumptions.

Since the economics of the reactor improve with a larger maximum temperature difference, we introduce this as a second variable on a contour plot. The reactor only exergy efficiency (Figure 4) is in the range of 0.96-0.98 for most of the operating space,

therefore milestone 1.3.2 is met for any economical design. The system efficiency of the base case system and the base case + turbine and future compressor are given in Figure 5. Increasing the maximum temperature difference reduces the amount of heat transfer surface area in the reactor but also reduces the exergy efficiency. The bottom right contours drop off very quickly due to very low compressor inlet pressures and some points are physically impossible due to the pressure drop across the sensible heat storage system requiring negative pressures.

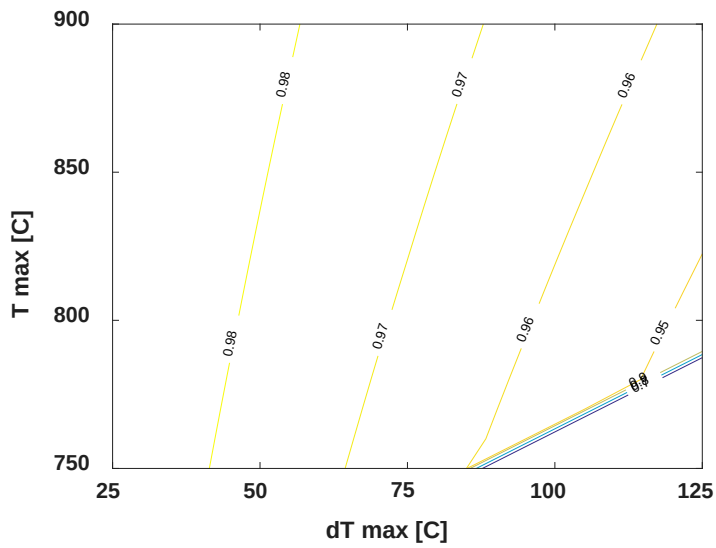


Figure 4: Bi-directional exergy efficiency of reactor only. For reference milestone 1.3.2 requires >0.95.

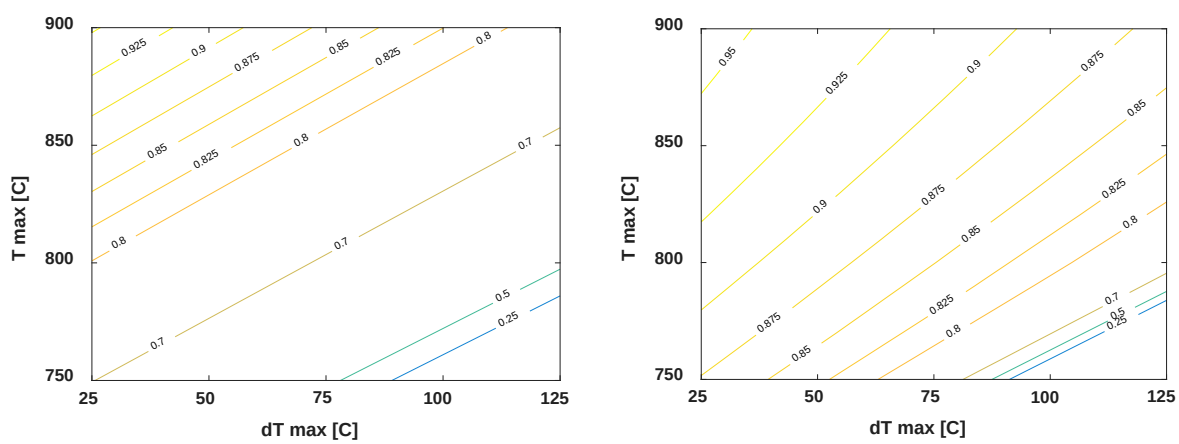


Figure 5: System exergy efficiency versus maximum temperature and maximum temperature difference in the reactor. Base case system (left), with the addition of a turbine and future compressor (right). Increasing the maximum temperature difference reduces the amount of heat transfer surface area in the reactor but also reduces the exergy efficiency.

Subtask 1.3.1 –Commercial Reactor Design

The requirements of the heat exchanger reactor are challenging because the temperature and pressure of the sCO2 are high at >720°C and 220 atm respectively, which puts materials limits on the HX. In addition, the sorbent material has

characteristically high open porosity for good mass transport kinetics and therefore poor heat conduction which requires large HX surface area and therefore high cost. We have taken a broad comprehensive approach to this problem and investigated a range of concepts for reactor designs, a summary of the analysis is given in Figure 7. The final recommended solution is to take the "separate intermediate HX and reactor" path meaning there is a low pressure shell and tube heat exchange reactor with a packed bed of sorbent on the shell side which circulates an low pressure intermediate HTF

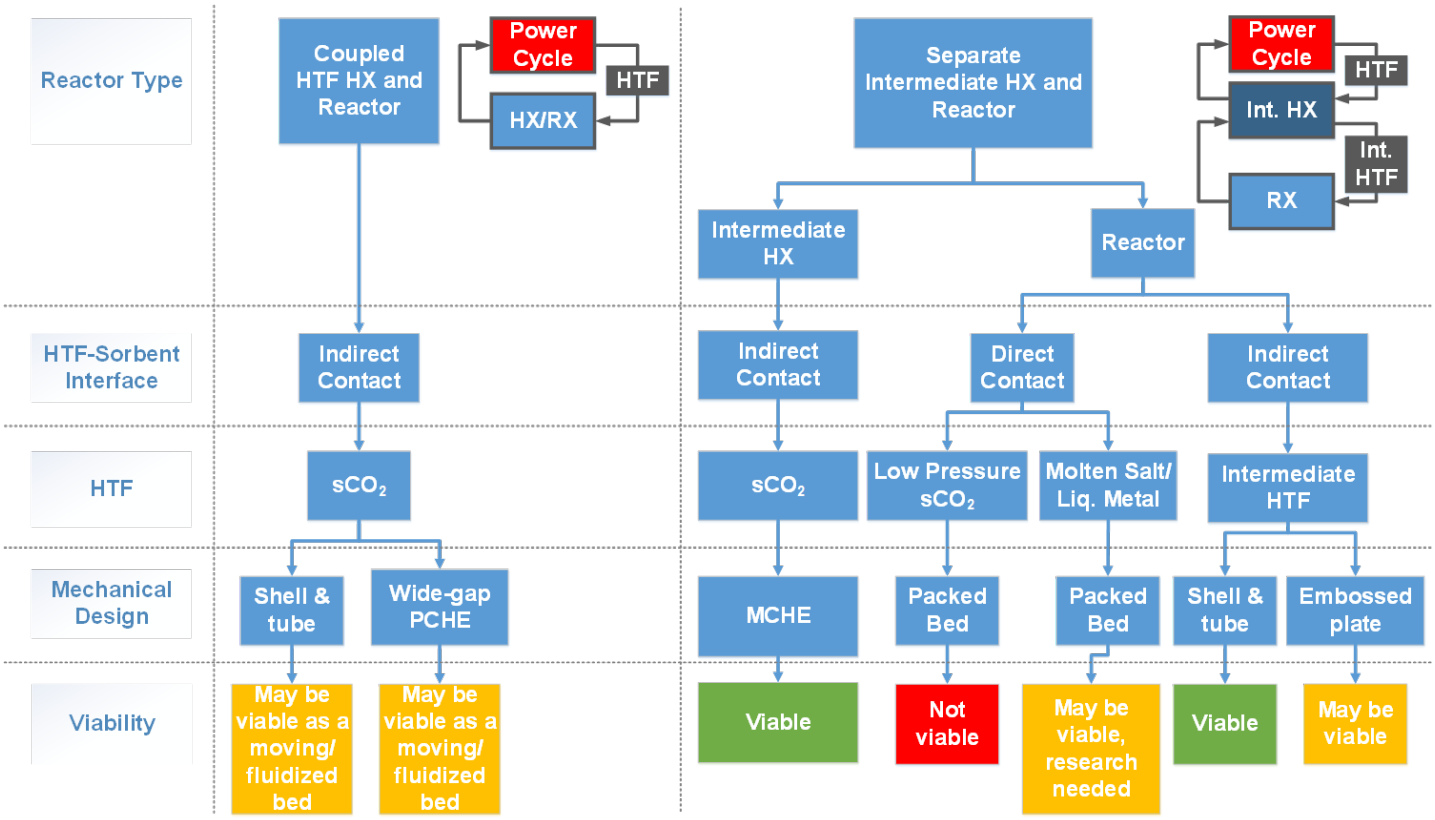


Figure 6. Reactor design selection flowchart

(molten salt, liquid metal) to a compact high pressure heat exchanger with the sCO2 from the power cycle. The following subsections give more details of the analysis which led to this conclusion.

Coupled heat exchanger reactor configuration

In this configuration high pressure sCO_2 flow channels transfer heat directly to a packed sorbent bed. The two HXRX types considered are tube and shell and diffusion bonded micro channel heat exchangers. The high design temperatures and pressure (>750°C, 220 [atm]) limit the candidate metal materials to just one: Inconel 740H which is rated by AMSE at up to 34.5 MPa at 800°C] and viable for high stress applications. Ceramic materials such as SiC and Mullite can be used at much higher temperatures (>900°C) and are available from manufacturers such as Ceramatec and Saint Gobain Industries.

Tube and shell (high ΔP)

We have been in direct contact with a tube manufacturer (Specialty Metals) to determine economics for thick walled, high pressure differential capable tubing using 740H. The cost is estimated at 926 [k$/m^3] for 740H tubing at an OD=3/4", we have used this cost basis for all calculations with 740H. A Model was created in MATLAB to evaluate the optimal tube spacing, rate of heat transfer and other HX dimensions as a function of tube OD. The model incorporates the effects of pressure and hoop stress as well as degradation and corrosion on piping specifications for the anticipated 30 year life under the proposed operating conditions. Results are plotted in Figure 7. The tube cost decreases with decreasing OD, if we assume that OD=¼" is the minimum practical size from a fabrication standpoint, then the minimum tube cost equals 14.3 MM$ for a rating of 750ºC and 28.4 MM$ at a rating of 800ºC. The total cost of the heat exchanger reactor is assumed to be higher by a factor of two, based on manufacturer input, therefore the total cost is 28.6 MM$ at 750ºC and 56.8 MM$ at 800ºC.

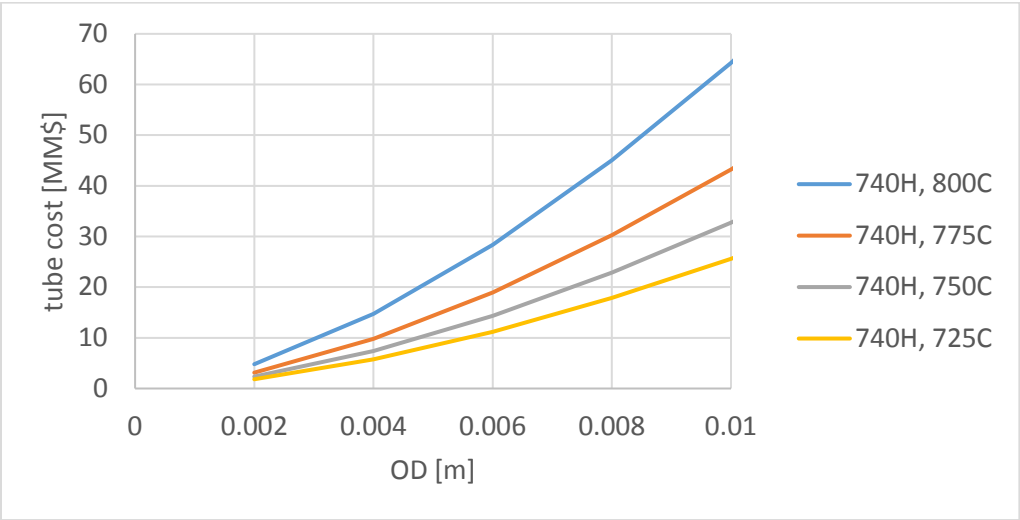


Figure 7: Tube cost versus OD for tube and shell reactor.

Diffusion bonded microchannel HX with fins

Diffusion bonded micro channel heat exchangers have been developed by many companies for sCO2 systems. The advantage is that they achieve very high rates of heat transfer and reduce the amount of expensive high temperature alloys. However, they are cost effective only when the rates of heat transfer are well matched, such as sCO2-sCO2 or sCO2-HTF.The conclusion is that solid conduction through the sorbent bed has characteristically low rates of heat transfer and therefore requires excessive heat exchanger surface area, driving up costs.

Separated reactor HX configuration

In this configuration the sCO_2 and sorbent are separated by a low pressure (2 atm) intermediate HTF (molten salt, liquid metal) with as-good or better heat transfer properties as sCO_2. The high pressure sCO_2-HTF heat exchanger will get much higher

overall rates of heat transfer and therefore be more compact and economical. The HTF will require a pump. The low pressure HTF-sorbent HX reactor uses low pressure tubing which will decrease costs.

High pressure sCO2-HTF HX

Both tube and shell and diffusion bonded plates are candidates for this HX. Inconel 740H is the metal alloy of choice up to 800ºC above that temperature would be a ceramic material such as SiC or Mullite. The lowest cost is a microchannel heat exchanger (MCHE) constructed from SiC or Mullite at a total cost of $11.8 M (Table 2).

Low pressure HTF-sorbent

The low pressure HX reactor can now use less expensive metal alloys and go to higher temperatures to meet the stress requirements. However the allowable thickness for corrosion largely determines the required thickness. It is assumed that the corrosion rate of the HTF and HX material is a low value of 10 µm/yr which is a target for Cl^- salt HTFs with very low concentrations of H_2O and O_2.

Tube and shell (low ΔP)

The low cost option would be to use 304H stainless steel at its maximum service temperature of 815ºC. At an OD=2 cm the tube cost would be <2 MM$ (Figure 8), therefore the HX reactor is estimated at 4 MM$.

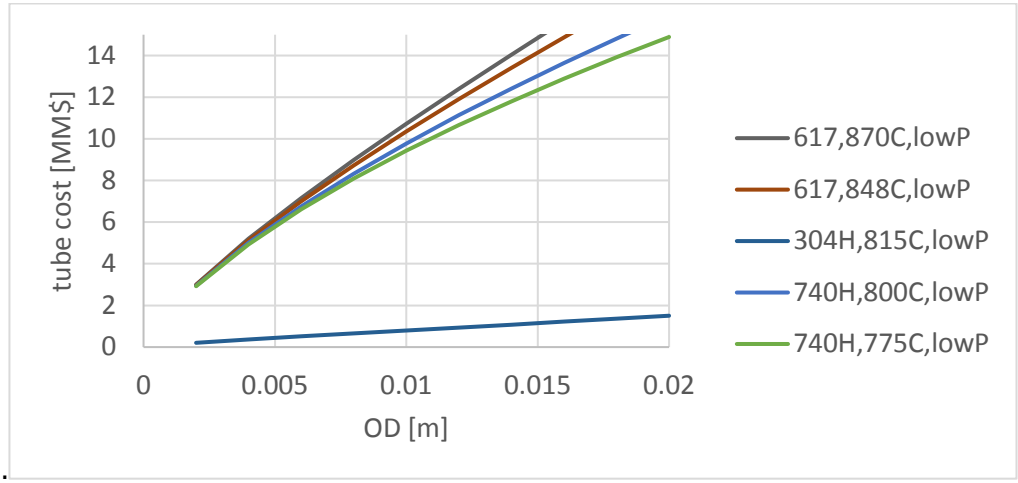


Figure 8: Tube cost versus OD for low pressure tube and shell reactor

Embossed plate (low ΔP)

Heat transfer plates can be welded into a flat plate. At the present we have estimated using the same materials cost basis as the shell and tube design. The cost of 304H comes in at <10 MM$, which is higher than the shell and tube but the embossed plate could have a potentially lower cost structure for fabrication, therefore this design is still viable and more analysis is needed.

Milestone 1.3.4 – Balance of Plant Cost

The milestone target represents the expected capital cost per installed kWh_{th} for the entire plant. It contains the cost of purchasing equipment, as well as any costs associated with installation, as well as contingencies, fees, land, etc. A Monte Carlo analysis was conducted to study the effects of the major cost drivers (primarily specific

pieces of equipment) on the overall capital cost. By achieving the targeted milestone success criteria it is expected that the plant would economically be able to deliver stored heat to a sCO_2 turbine system for electricity generation.
Based on the simulation, the total capital cost for the reactor and BOP (including 36% contingency, fees, etc) is $36-42 /kwh with up to 50% reduction in future development costs. The initial design for the thermal storage system had an integrated heat exchange reactor (HXRX) operating at sub-atmospheric pressures, while the gas storage was operated at 25 bar. This required pulling a vacuum on the reactor then pressurizing the gas to 25 bar. Some iterations of the HXRX had an integrated HX-reactor, Figure 9 shows the ASPEN simulation PFD of the system, while other iterations had the reactor split into a high pressure compact HX and a low pressure HX reactor with the two connected by some intermediate heat transfer fluid (He, liquid Na, molten salt, etc).

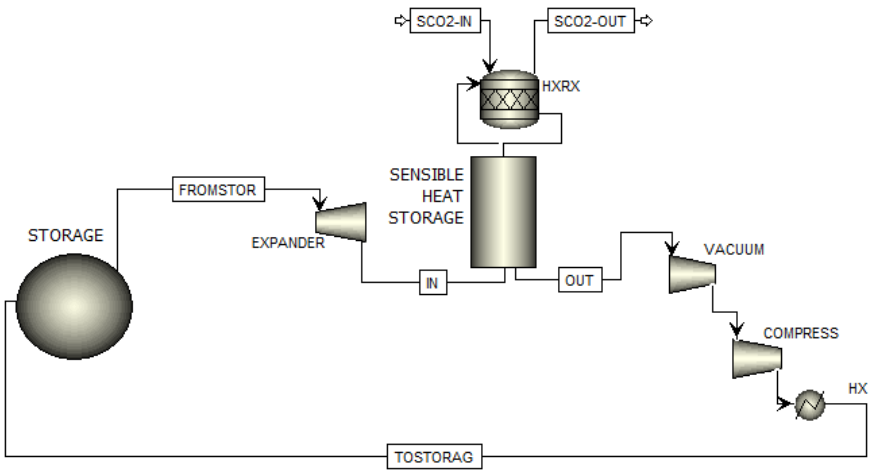


Figure 9: ASPEN PFD of Original System Design

After revisiting the calculations for the HXRX, it was found that the material of construction needed to be changed to 740H or other high temperature alloy rather than 304L, which significantly increased the costs. Table 2 shows how the new values for the integrated HXRX compares with some of the quotes for the bifurcated system received from vendors. Two quotes were based on a helium heat transfer fluid, while the one quote was based on a liquid sodium heat transfer fluid. It is expected that if an alternative denser heat transfer fluid could be used, then the size and cost of the other helium HTF heat exchangers could be reduced (alternatively, if the dT across the reactor could be increased, it would also decrease the size and cost of the HXs.

Table 2: Installed Reactor System Costs, column highlighted in orange represents the recommended solution.

HX+Low Press. HXRX or High Press. HXRX	Reactor Cost w/ Diffusion Bonded HX (He HTF)	Reactor Cost Shell-Tube (He HTF)	Reactor Cost w/ Ceramic HX (Na^+ HTF)	740H Combined HX Reactor (Shell & Tube)	Moving Bed Reactor
Blower/Magnetic Drive	$30,786,000	$30,786,000	$767,584	NA	NA
High Pressure HX	$45,600,000	$104,000,000	$7,000,000	NA	NA
HX Reactor	$4,000,000	$4,000,000	$4,000,000	$42,000,000	$8,400,000
Particle lift, etc	NA	NA	NA	NA	$5,000,000

HX+Low Press. HXRX or High Press. HXRX	Reactor Cost w/ Diffusion Bonded HX (He HTF)	Reactor Cost Shell-Tube (He HTF)	Reactor Cost w/ Ceramic HX (Na^+ HTF)	740H Combined HX Reactor (Shell & Tube)	Moving Bed Reactor
Total Reactor Costs	**$80,386,000**	**$138,786,000**	**$11,767,584**	**$42,000,000**	**$13,400,000**

Excluding the HXRX, the first pass at the capital cost estimate done with ASPEN for the balance of plant (BOP) showed that the built in equipment cost for this configuration was much too high to meet the cost targets. Vendors were contacted to verify if the ASPEN estimates were correct or to provide an alternative value. A rough pressure sweep analysis was conducted in ASPEN to find other potential alternatives. Table 3 shows the results of the pressure sweep rough analysis. The analysis identified atmospheric gas storage in inexpensive vinyl buildings as a potential alternative.

Table 3: Results of pressure sweep analysis for solar storage BOP costs, column highlighted in orange represents the recommended solution..

BOP	ASPEN Model (25 bar gas storage)	1 bar gas storage (metal storage)	1 bar gas storage (vinyl storage)	7 bar gas storage	11 bar storage liquid
Sensible Heat Storage	$1,100,000	$1,100,000	$1,100,000	$1,100,000	$1,100,000
Vacuum Pump	$20,000,000	$20,000,000	$20,000,000	$20,000,000	$20,000,000
2-Stage Compressor	$22,190,000	NA	NA	$17,690,000	$19,650,000
Storage Vessel	$49,505,000	$2,149,100,000	$28,000,000	$89,346,000	$9,100,000
Expander	$12,982,400	NA	NA	$3,020,200	$4,503,600
Compress. Cooler	$1,590,000	$1,590,000	$1,590,000	$1,590,000	$1,590,000
BOP Plant Cost w/o HXRX	**$105,777,400**	**$2,171,790,000**	**$50,690,000**	**$132,746,200**	**$55,943,600**
HXRX Cost	$11,767,584	$11,767,584	$11,767,584	$11,767,584	$11,767,584
Contingency & Fees	$42,316,194	$786,080,730	$22,484,730	$52,024,962	$24,376,026
Total Plant Cost	**$159,861,178**	**$2,969,638,314**	**$84,942,314**	**$196,538,746**	**$92,087,210**
$/kWh$_{th}$	**$79.93**	**$1,484.82**	**$42.47**	**$98.27**	**$46.04**

Figure 2 shows the simplified schematic for the 1 bar gas storage case. Since the gas is not compressed, the equipment required for compression and expansion are eliminated. However, the storage volume is ~25 times larger. Using conventional metal tanks was extremely expensive and not realistic, however, large inflatable building structures provided an attractive alternative. The costs associated with the 1 bar gas storage with vinyl storage has shown to be the lowest capital cost option. However, there remains great potential for improvement in this case, as well as potential impacts that have not been fully evaluated. The vacuum pump specified for all the cases listed 32 banks of smaller pumps. Additionally, the vinyl storage was also provided through a quote for 16 half-dome structures (d=100', L=650', h= 50'). Both of these items, but especially the vacuum pump could see cost reductions through consolidation. Using a scaling law to reduce the number of banks of pumps down to just one bank of 12 pumps could potentially reduce the cost by 35-75%. It is estimated that the cost can get as low as $19.50/kwh if multi-unit items are scaled up to a single item.

A Monte-Carlo simulation with 30,000 cases was run for this scenario and plant design to determine the distribution of balance of plant capital construction costs if the equipment costs underwent some changes in cost. Table 4 shows the input variables

and distributions as well as the expected results. For the simulation, the storage and vacuum pump costs were simulated using a half-normal distribution with a max value taken from the pressure sweep study, while the heat exchange reactor used a normal distribution with a 8.5% standard deviation, and the BOP equipment, contingency, and fees used a normal distribution with a standard deviation of 5%.

Table 4: Monte-Carlo Simulation of installed equipment costs.

	Vacuum Pump	Storage	RXHX	BOP	Cont & fees	Total Cost ($/kWh$_{th}$)
Base value	$20,000,000	$28,000,000	$11,767,584	$2,690,000	$22,484,730	$ 42.47
Variance	$4,000,000	$3,000,000	$1,000,000	$134,500	$1,124,237	
Case	Vacuum Pump	Storage	RXHX	BOP	Cont & fees	Capital Cost ($/kWh$_{th}$)
Max	$19,999,312	$27,999,871	$15,481,863	$3,250,576	$26,365,874	$ 43.99
75%	$18,733,759	$27,011,087	$12,446,887	$2,778,450	$23,232,743	$ 40.89
Average	$16,801,978	$25,576,717	$11,774,613	$2,689,712	$22,472,189	$ 39.66
25%	$15,357,347	$24,498,036	$11,077,073	$2,599,972	$21,702,210	$ 38.60
Min	$2,796,255	$15,920,562	$8,279,126	$2,103,101	$18,387,259	$ 32.07

The large size of the plant has caused the overall capital cost estimates for the plant to exceed the milestone targets, however, this is largely driven by the current scale of current equipment. The utilization of many pumps and storage vessels has caused the plant costs to increase linearly to achieve the large scale of the storage facility. It is anticipated that as the equipment scales to meet the size of the plant and as the design of these technology improves to meet the specification of the plant that the overall capital cost can be decreased by up to 50%. This would bring the capital cost of storage down to about $20/kWh$_{thermal}$ and would be near the target value of the milestone.

Task 2.2 Sorbent Recovery

Sorbent degradation or sintering is known to occur via two mechanisms: 1) grain growth and 2) pore closure. Stabilizing phases were added to reduce CaO grain growth and potentially arrest it altogether via Zenner pinning and phase separation of the composite sorbent. CaO has a very high melting temperature (2572°C) and is very stable in inert atmospheres when mass transfer is controlled by thermally activated vacancies and dislocations through the grain or at grain boundaries. However chemical adsorption via CO_2 and H_2O increase the surface mass transfer by orders of magnitude. In general, lower temperatures and lower P_{CO2} and P_{H2O} decreases sintering in CaO. The sorbent material is known to operate very near chemical equilibrium at all times as is evidenced by experiments with CO_2 equilibrium pressure and thermochemical modeling using HSC 9.0 and Factsage Web, which both predict the chemical compositions observed by XRD. If grain growth and pore blockage can be arrested or reversed then material lifetime can be extended indefinitely.

Subtask 2.2.0: Sorbent degradation model

TGA high cycle data is the most practical indication of a high performance sorbent and is appropriate for quantitative comparison, however it does not give an absolute value on sorbent lifetime. To give a lifetime prediction with greater certainty would involve combining TGA data with analytical testing of the microstructure (crystallite size), chemistry and porosity of the materials which is out-of-scope for this project.

Through experience we have converged on a standard TGA method for quantitative high throughput sorbent testing: isothermal at 843 °C with a 30 min carbonation at 50% CO_2 followed by a 5 min decarbonation at 2.83%. This is 123°C above the nominal system design temperature of 720°C. Many CaO-based sorbents in literature have shown an asymptotic approach to a "residual capacity" value in the high cycle limit. Our own experiments have also shown that a residual capacity seems to be a good characterization for natural coral samples however not for the synthetic CaO-based sorbent developed under the ELEMENTS project (Figure 10).

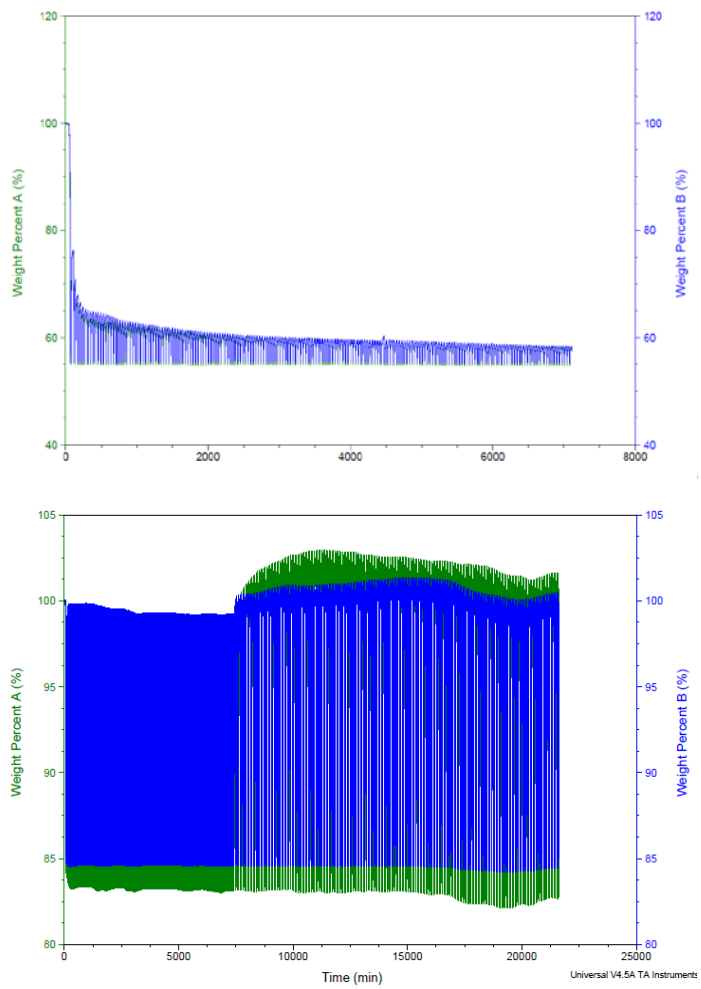


Figure 10. Long duration testing in the TGA use the standard method for accelerated testing. Top figure:natural coral powder (green), and chunk (blue) exhibit an asymptotic limit to a residual capacity value. Bottom figure: Long duration testing of SR-made 2-1 sorbent (blue) and 2-1 sorbent from phase I in (green) in the TGA, 581 cycles, the longest to date.

Long duration, accelerated testing in the TGA was performed on PCI-made 2-1 sorbent and SR-made 2-1 sorbent (Figure 10). The first 209 cycles were conducted under the standard test conditions, the next 372 cycles the carbonation time was increased to 60 min, while the other parameters were unchanged. This is our highest cycle dataset to date, at a total of 581 cycles at accelerated conditions. The weight gain capacity between the two samples were nominally equivalent, varying from 17-23% and showed high resistance to degradation. It may be true that the material is already at its residual capacity.

The SR-made 2-1 sorbent did exhibit a clear asymptotic approach to a residual value when tested under more severe testing conditions: carbonated at 830 °C with 50% CO_2 for 30 mins and decarbonated at 900 °C with 3% CO_2 for 30 mins. After 54 cycles at the above mentioned conditions, sorbent capacity decreased from 40.29% to 19.69% (Figure 11).

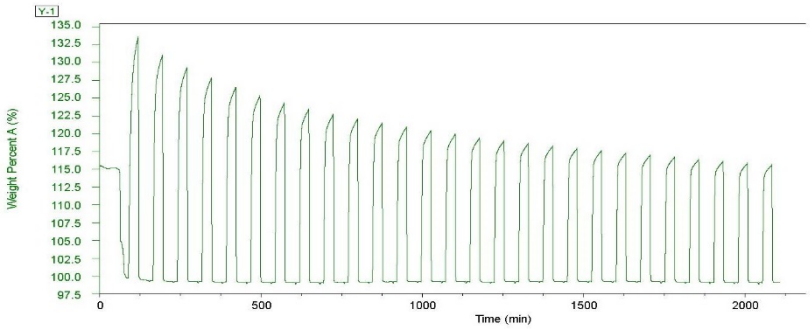


Figure 11. Accelerated aging of SR-made sorbent in the TGA for 54 cycles under the following: carbonation at 830 °C with 50% CO2 for 30 mins and decarbonation at 900 °C with 3% CO2 for 30 mins.

Milestone 2.2.1: Steam recovery

The Bench scale system was converted to operate using steam, and cycles were performed to control the hydroxide reaction and accurately measure the resulting weight gain. Steam cycles showed a very consistent weight gain of 13.68±0.55% (T=1.771). No statistically significant (p=0.6) degradation was observed over the 13 cycles hydroxylation cycles. Milestone 2.2.1 was achieved and the main conclusions are as follows

1) Switching from CO_2 to steam and back can be controlled from an operations standpoint.
2) The kinetics of the hydroxide reaction are fast and the reactor is heat transfer limited, similar to the carbonation reaction.
3) This particular test was unsuccessful in increasing the capacity of CO_2 reaction (Table 5); however, there could be a number of reasons for this. The final evaluation of the efficacy as a sorbent recovery process still requires more work to optimize through controlled lab experiments.

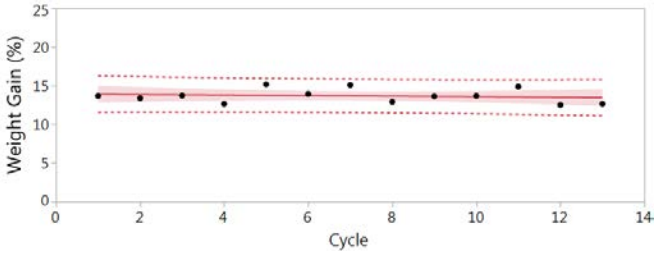


Figure 12 Steam cycles of calcium based sorbent show consistent water absorption at 13.68±0.55%. No statistically significant (P=0.6) degradation was observed.

Table 5 Summary data of the steam cycles, and the pre- & post-steam CO_2 cycles.

	Avg Wt. Gain (%)	95% C.I. (± %)	Wt. Gain (mmol /g)	T-Value	Total Cycles	Degradation (%-abs. per 100-Cycles)	Fit	F-Ratio	P-Value: Intercept	P-Value: Slope
Last CO_2 Cycles prior to steam cycles	8.73	0.143	1.98	1.677	49	0.16535	W = 8.6850217 + 0.0016535*C	0.1629	<0.0001	0.6883
Steam Cycles	13.68	0.55	7.59	1.771	13	-3.7955	W = 13.943363 - 0.037955*C	0.2938	<0.0001	0.5986
Post-Steam CO_2 Cycles	2.245	0.028	0.51	1.740	17	3.82821	W = 1.7721326 + 0.0382821*C	268.6	<0.0001	<0.0001

Task 2.3 Gas storage

Subtask 2.3.1: Gas Storage

Membrane structures

New gas storage systems have led to potentially substantial cost savings. Two designs have been proposed, one achievable with current technology achieves a 47.9% cost reduction, the other would require additional research, but could represent >77% cost reduction. The first design enables addition of over 48,000m^3, or ≈ 73.8% more gas per building. The cost per structure, based on commercially verified estimates, would be $1,906,000 and would store 113,000m^3 of gas. 9 structures would be needed to store 1,000,000m^3 of gas. Total gas storage cost would be 17,200,000, or $16.91/m^3. A savings of $10,800,000 over the lowest previous estimate. Additional modifications to this design enable storage of ~ 143,000m^3 of gas, and cost $2,082,000+reinforcement costs. Seven structures would be needed for a total system cost of $14,600,000. A further savings of $2,300,000.

A second, proprietary design concept enables proposed system based on a structure being inflated with the CO_2 using pressure of approximately 1-1.25 inH_2O and a maximum temperature of 60°C. Total cost would be $616,000 – $676,000 per structure. Total cost for 9 such structures, would be just $5.58 million dollars, or $5.49/m^3.

Structure Placement and Size compared with CSP Molten Salt

For a modern 2GWh$_{th}$ two tank molten salt TES system each tank may be ~150ft in diameter, and ~50ft tall, the total footprint for a two tank system including pumping and piping might be 450x150ft. This valuable space must be placed central to the power tower, and takes up space better used by heliostats, which are most effective close to the tower. By comparison, the membrane gas storage structures can be placed at a distance, beyond the heliostat field, and connected to the tower by low-pressure, low temperature piping. It is even possible that a single remote site could supply gas storage to multiple power towers.

Furthermore, the structures could be arranged around the field so as to create a wind break for the heliostats. Most research on wind breaks for Heliostat fields to date has examined porous fences of comparable height to the heliostats themselves, and significant reductions of

detrimental wind effects have been observed at the field edge. These structures though are 50ft tall and the reduction may penetrate further into the field.

CO_2 loss by permeation through the membrane

The cost of CO_2 make up by permeation can be neglected for the commercial system. Given the permeability of the membrane material (36 $cm^3/(m^2*day)$, measured by the manufacturer) the total CO_2 loss is 0.32 % of the total inventory per year or 9.54% over 30 years.

Task 2.4: Pilot system design

Subtask 2.4.1: Reactor specifications, modeling

Sorbent Crush Strength - The crush pressure of the SR-made 2-1 sorbent under room temperature conditions was measured to be 77 [MPa], which is equivalent to a column of sorbent with a height of ~8000 [m]. Therefore the crush pressure will not limit the design of the pilot scale reactor.

During the phase I review and phase II negotiations the task of pelletization of the sorbent for a commercial scale reactor was deemed a development task for industry, and out of scope for the remainder of the Apollo project. The pilot reactor will be designed with a minimum permeability to allow sufficient mass transfer, for a gas length path of 3-6 [cm] the corresponding target particle size is 100-200 µm. The SR-made 2-1 sorbent was measured (sifted with screens) to have a d50 particle size in the range of 75-125 [µm] (d44=75[µm], d79=125 [µm]). After a simple procedure of hydration, pressing into a large pellet die, and then breaking apart, the particle size was increased to d6 = 125 [µm]. In addition the larger particle sorbent had a slightly higher CO_2 capacity than the original smaller particle sorbent, which is consistent with previous TGA results that a hydration treatment of sorbent at room temperature increases the CO_2 capacity. The permeability of the SR-made 2-1 sorbent (original, smaller particle size) was measured via a custom built testing system to be 4.7e-13 [m^2] which corresponds to a calculated effective particle size of 63 [um] which is consistent with the previous d50 measurement. This demonstrates we have the characterization equipment, modeling tools and sorbent which meet specifications for the pilot scale reactor.

COMSOL Modeling

Multiple finite element models for the pilot reactor were created in COMSOL. The geometry was manually optimized and finalized in a two-dimensional model, with coupled heat, mass transport and chemical reaction kinetics. The governing equations and domains of the model are identical to what has been described in previous reports, with some improvements to computational efficiency. We began with a 3-channel reactor design, but settled on a 7-channel design to increase the charging rate of the system (decarbonation). Figure 13 illustrates the 2D mesh for the modeled region which is a 1/12 wedge of the entire 7-channel reactor. Figure 14 plots the extent of reaction contours after 5.5 hrs of charging which shows the regions that are slowest to decarbonate. The carbonation conditions held 720°C at the HTF (heat transfer fluid) and provided a constant pressure to the outside of the reactor at a pressure corresponding to an equilibrium at 795°C. The decarbonation conditions held the HTF at 695°C and an external

pressure of 0.005 atm (506 Pa). Figure 15 plots the average extent of reaction for both discharging (carbonation) and charging (decarbonation). The time to reach 90% of completion is 1.8 hr and 4.4 hr respectively. Figure 16 plots the heat flux during these periods. Based on the results we expect the pilot system to achieve all milestones for budget period II.

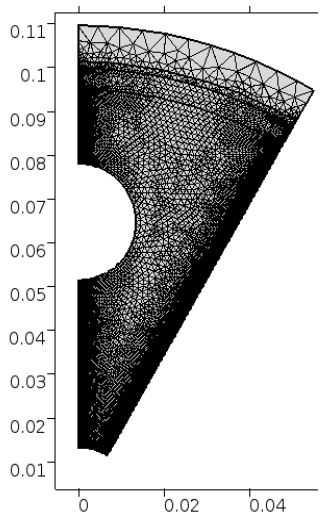


Figure 13. 2D Mesh of pilot reactor.

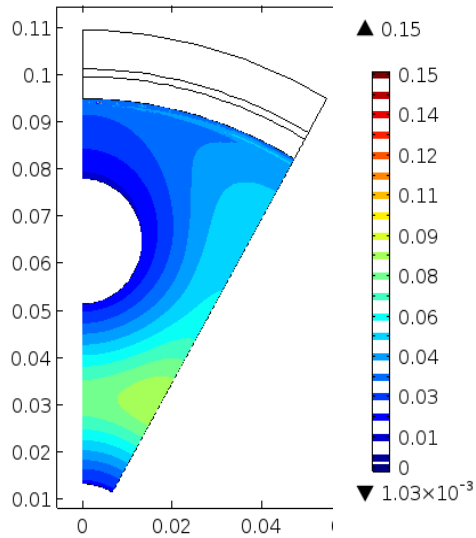


Figure 14.Extent (X) of reaction after 5.5 hr of charging (decarbonation). X=1 is fully

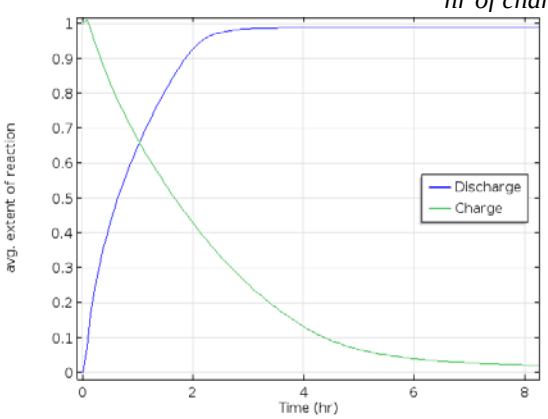


Figure 15. Average extent of reaction vs. time for both discharge (carbonation) and charge (decarbonation) without controls.

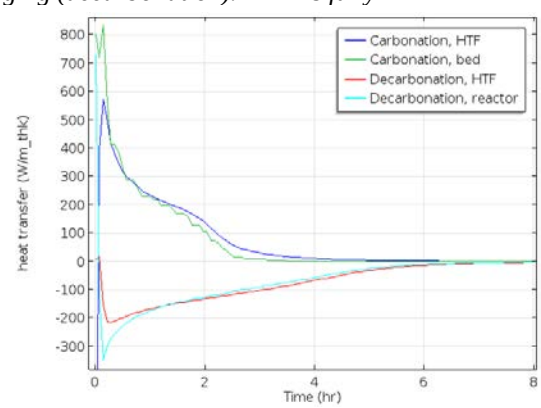


Figure 16. Heat transferred at the HTF and throughout the bed during uncontrolled carbonation and decarbonation.

Thermal Performance & Modeling

A 3D-FEA model of the reactor was assembled in COMSOL to inspect stress and strain on the reactor. Heat transfer, and volumetric heat generation/absorption by the sorbent were simulated, and both carbonation and decarbonation steady states were analyzed. During carbonation, inlet HTF temperatures were 700°C. Maximum sorbent temperatures were calculated at 723°C, and the HTF fluid was raised to 712°C before exiting the reactor Figure 17..

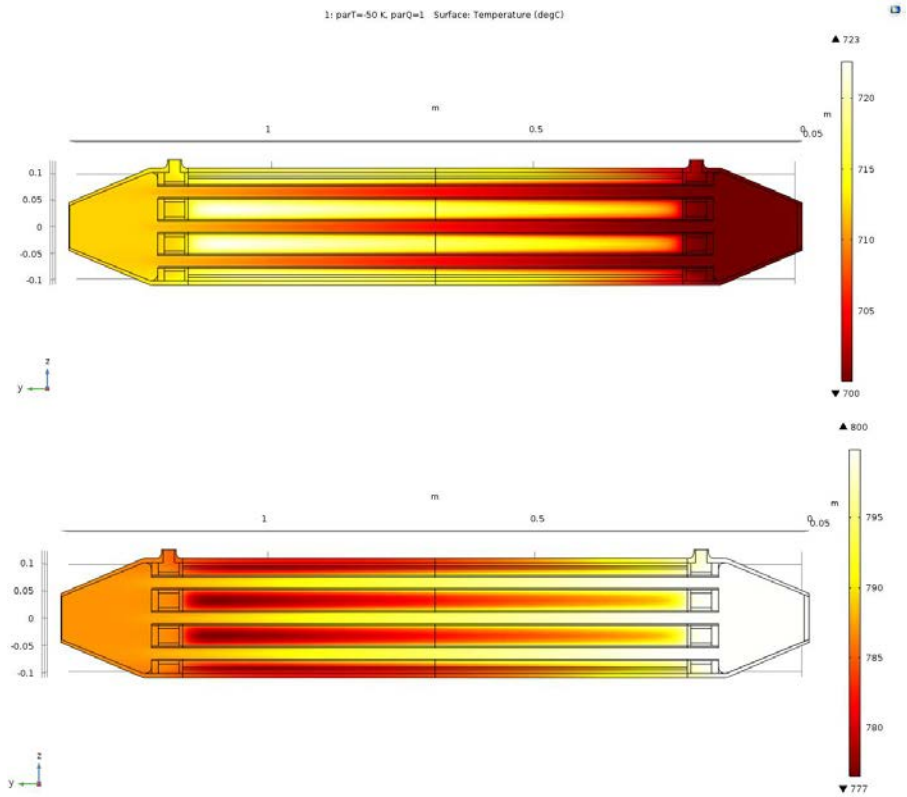


Figure 17. Steady-state temperature profile during carbonation (top) and decarbonation (bottom).

During Decarbonation, inlet temperatures were 800°C. This is above the recommended operating temperature of 720°C, but provides a harsher test of the reactor, and ensures greater flexibility during testing. Temperatures in the sorbent reached a minimum of 777°C, and the HTF fluid left the reactor at 787°C. Based on the strain analysis conducted on the assembled reactor, the greatest strain range, i.e. difference in strain between carbonation and decarbonation, appears to be 0.788% by volume. Based on material characteristics published by Special Metals, makers of Incoloy 800HT, this equates to an expected cycle lifetime of at least 2,500 cycles.

Stress analysis assumed sharp corners and no tolerances, meaning worst case approximations. Due to these choices in model characteristics the maximum stress was 6.58ksi which would deliver a 3,000 hour life.

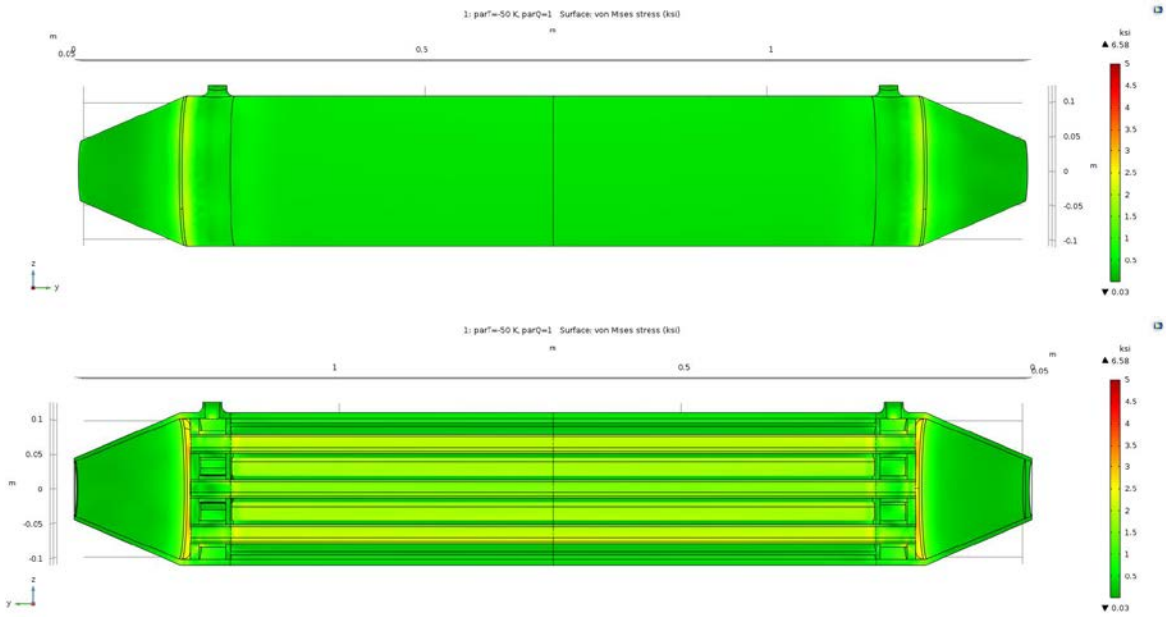


Figure 16. Overview of stress on outer shell and inside of reactor.

The model shows that the major stress concentration is at the interface between the tube collars and the external manifold plates. This is due to the greater linear thermal expansion in the tubes caused by their high temperature relative to the shell. This is a worst case approximation as the actual reactor will have filleted welds and a greater tolerance between the collars and the plate. A conservative estimation with filleted welds alone is a reduction of 1.38ksi to 5.2ksi leading to a 10,000 hour life. Additionally, indications from vendors are that simple creep or thermal fatigue failure at a fusion line between filler and base have not been observed. The stress in the shell of the reactor was less than 2.5ksi, a greater than 100,000 hour life for the shell, meaning there is little concern of a shell failure.

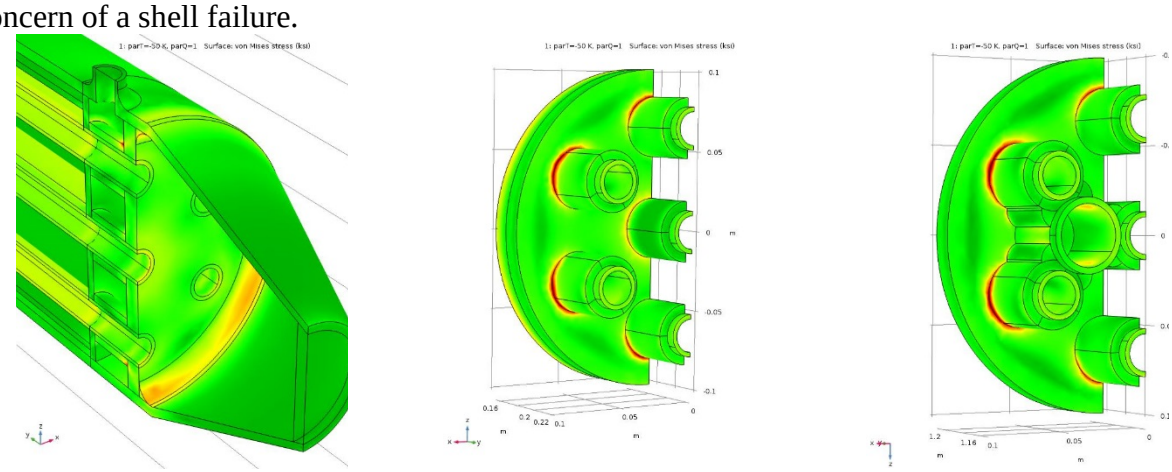


Figure 17. Detail of maximum stress locations. High stress is created at the join between the tube collars and manifold plate. This stress is caused by the HTF tubes bowing outwards due to greater thermal expansion relative to the shell.

Subtask 2.4.2 – Reactor mechanical design

Based on discussion after the Year 1 Quarter 4 review, a smaller 4 kWh reactor design was chosen for the pilot scale system. An 8” shell and 3/8” tubes were chosen based on required sorbent volume, tube spacing, gas flow rates, gas flow velocity, and cost. The design was fully modeled and drawings rendered.

Figure 18 is an overview of reactor components and assembly. From left to right, the first view is an elongated exploded view showing the overall reactor. The second view is a sprawled out component layout. Next the view is made transparent, and the last two views are the fully assembled reactor with a cutaway revealing how the insides should look once assembled.

The first part of the assembly is the conical reducer. This is the piece that attaches directly from the 304ss tubing into the Incoloy 800HT body of the reactor. This part is to be directly welded onto the outer body (shell) of the reactor itself, and diffuses air through the heat transfer tubes.

The nomenclature for the naming of the manifold parts are as follows. In the overall design there are 2 manifolds (A,B) that differ only in that the first (A) has a port to fit a plug to load and unload sorbent into the reactor while the second (B) does not. Each manifold is then split into two parts by number (1,2). The number indicates the element that is more peripheral (1), or more central (2).

Originally, the central elements (A2 & B2) were to be made of Incoloy 800HT, however perforated plate of this material would have to be custom machined, with a delivery time of up to 4 weeks. To save time and money, and given that the elements were not load bearing, perforated 304 SS sheeting was used in lieu of Incoloy. The perforations allow carbon dioxide to flow from the CO_2 inlet or outlet void between the two plates into the reactor and sorbent.

The heat transfer tubes will be ¾” Sch. 40 seamless pipe (OD: 1.050”, wall thickness: 0.113”) made from Incoloy 800 HT. Tube collars were added to reduce stress at the join between the tubes and the outer tube manifold plate. COMSOL stress analysis showed these points were areas of high stress, due to the thermal expansion.

A plug is added to manifold A, adjacent to 3 of the collars between A1 and A2. Like the tube collars the plug is meant to reach from the internal face on A2 to the external face of A1 and welded externally. This plug will allow the sorbent to be loaded into the reactor, and extracted by means of a soil auger after testing is completed.

The same perforated metal will surround the sorbent, improving the flow of gas throughout the bed by creating a gas channel along the outer perimeter of the shell. Wire cloth will prevent leaks.

The outer shell of the assembly is an 8” Sch. 40 seamless pipe (OD: 8.65”, wall thickness: 0.322”) of Incoloy 800HT with two ports (one at either end) on opposing sides.

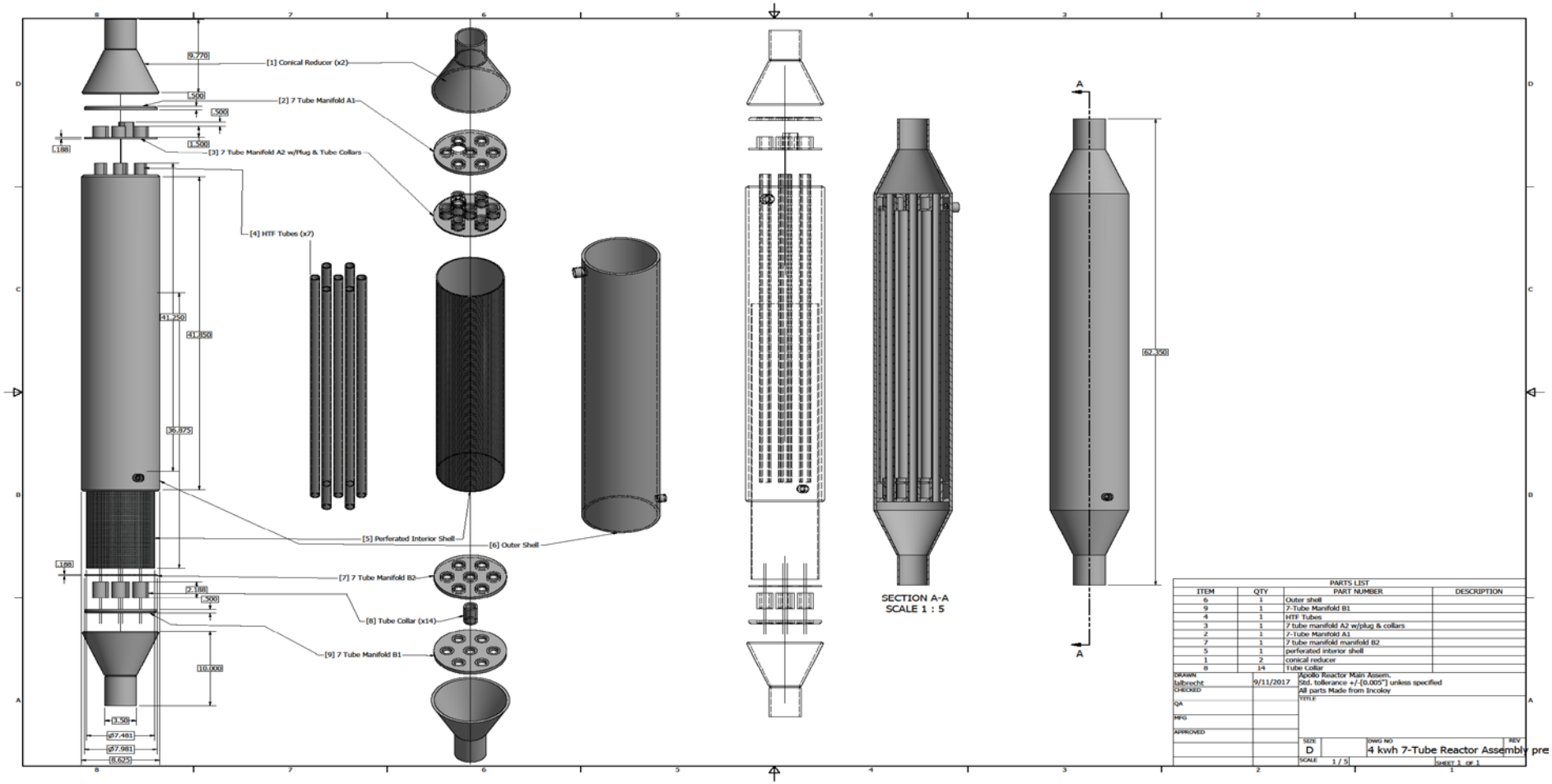


Figure 18. Exploded view of reactor design

Figure 18

Subtasks 2.4.3 & 2.4.4: Pilot system balance of plant

The pilot system layout differs from the bench-scale system layout in several key aspects. First, the components will not be assembled onto a single skid. Instead, components have been segregated into functional groups, such as the HTF furnaces, the CO_2 furnace, and the low pressure CO_2 MFCs. Modules are designed to pack closely, minimizing the length of hot transfer piping. Electrical connections between modules will be handled by pre-wired quick-disconnect junction boxes. This ensures electronics only need to be connected once, even between shipments.

Controls were implemented on a National Instruments CompactRIO (CRIO) platform. The CRIO platform is a high-performance, industry tested solution for advanced, reliable, and connected control systems. CRIO controllers feature two processing units, a real-time processor for communication and signal processing and (2) a field programmable gate array (FPGA) for implementing high-speed control and custom timing and triggering directly in hardware. Sensor components connect directly to the CRIO platform, eliminating the need for separate subsystems. The CRIO controller chassis is expandable, allowing the system to grow with and adapt to future sensor and control needs.

The simplified PFD shown in Figure 19 is intended to provide the DOE with a quick-reference guide to the system and its standard operating conditions. Pressure, temperature and flow rate are indicated in place along with major components. Fully detailed PFDs and P&IDs are available upon request.

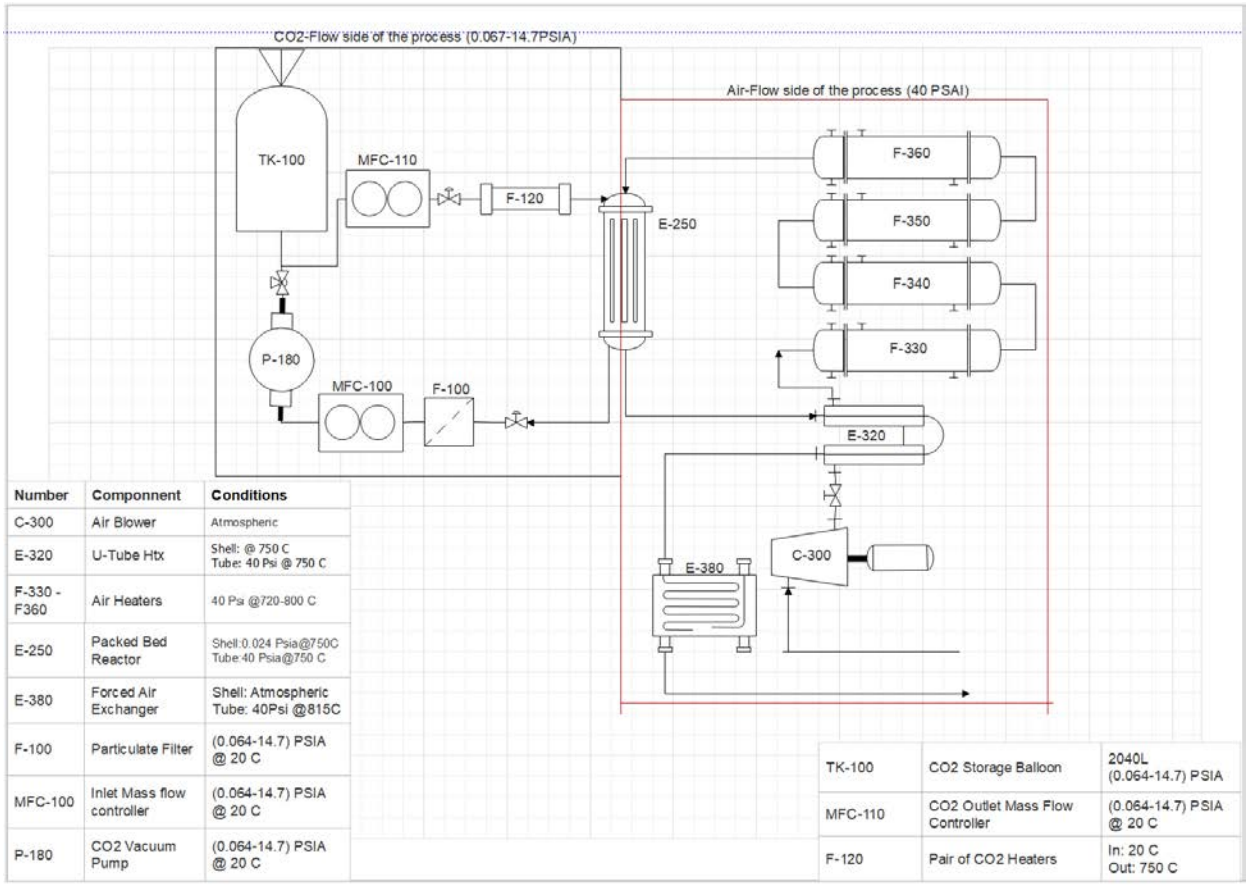


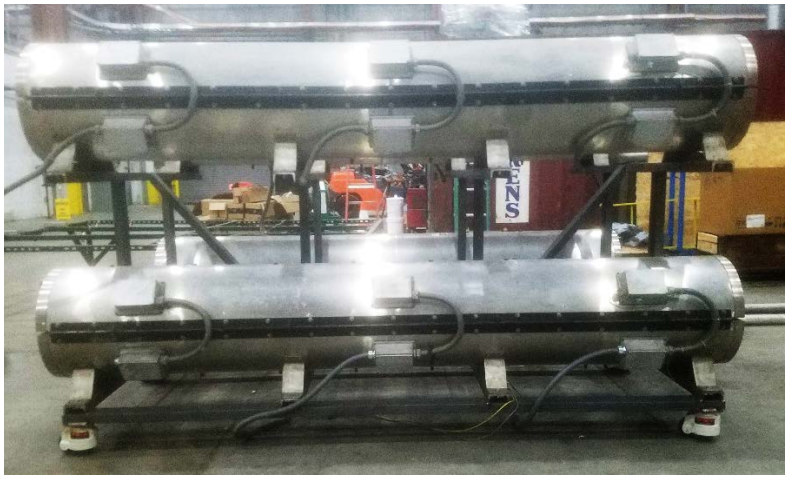
Figure 19. Simplified block flow diagram of the pilot system. PFDs and P&IDs are available upon request.

Task 2.5: Installation, commissioning, and testing

The figures below illustrate the construction of the major system components.

(a)

(b)



(c)

Figure 20. Constructed skid components a) bladder, b) air HTF recuperator c) primary air HTF furnaces

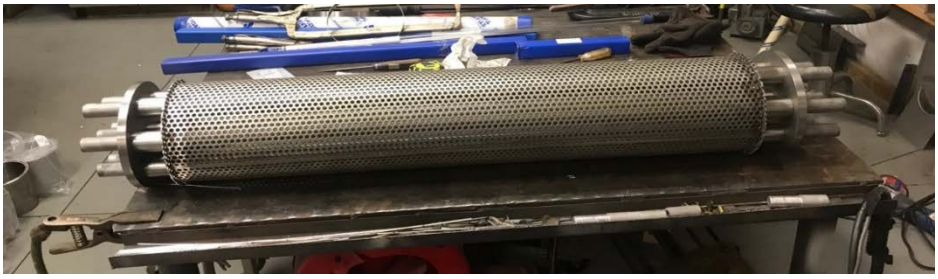


Figure 20. 7-channel shell and tube reactor.

Thermal Expansion bellows are present on all long runs of high-temperature piping

CO_2 heating elements, filled with ball-bearings for improved heat transfer.

Detail of the sorbent fill port

Pitot tube pressure sensor and flow meter, with digitally controlled butterfly valve for flow control

Front facing view of the Reactor and heaters

Heat trace is being provided by high temperature clamshell heaters. These are less likely to malfunction than the MI cable used on the previous skid.

Figure 21. Prototype system pictures before insulation

Figure 22. Electrical controls cabinet

Sorbent for prototype system

The recipe of sorbent 5.5 used in the prototype system is proprietary.

SR completed a 30 kg large batch using a co-precipitation method. The main components are a tank with conical bottom, impeller, pump, and positive pressure 1-micron. The co-precipitation has been successful with manual pH controls, and in good agreement with lab-scale synthesis. In the future a pH control system will be added which is more critical for applications such as catalyst production. Control of solids transport through the pump and washing procedure in the filter bag has been successful. Sorbent has been washed and air-dried into clumps, oven dried, then crushed and screened into sized of 300-5000 um. Thus we have obviated the need for separate pelletization step.

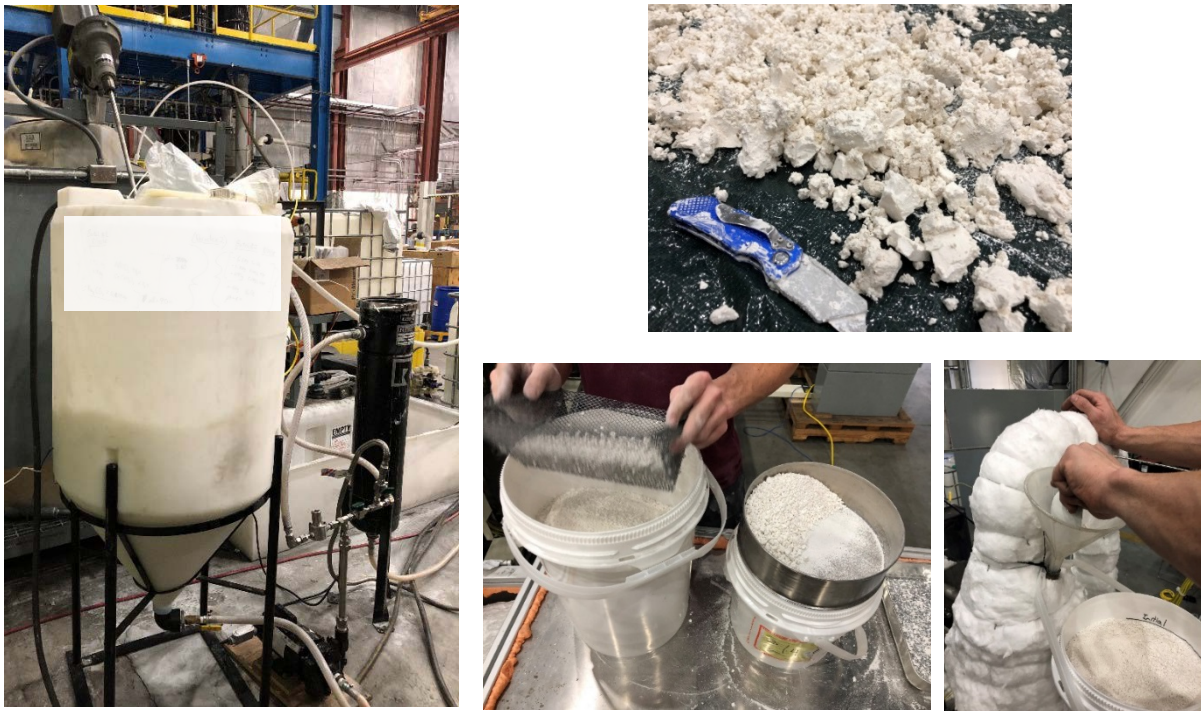


Figure 23. Large batch synthesis of a CaO sorbent for TCES. Main components are a tank with conical bottom, impeller, pump and positive pressure filter. Sorbent washed, air dried, oven dried and screened to 300-5000 µm.

Milestones 2.5.1 – 2.5.6 Prototype System Commissioning

The basic operations of the energy storage system were demonstrated for carbonation (discharging) and decarbonation (charging) over short time periods. Excellent control of the CO_2 mass balance across the reactor was achieved with mass flow controllers and the basic operation of the level control of the CO_2 gas bladder was achieved. The system was apparently free from leaks and operated continuously for 18 days with no mechanical failures, thus meeting milestone 2.5.5. The major shortcomings of the system had to do with the controls which prevented us from deep cycling and or reaching high cycles. The PLC (National Instruments CompactRIO) was very stable with moderate system temperatures < 700 ^{o}C, however above ~700 ^{o}C it would constantly loose connection, requiring a system restart. Extensive troubleshooting was applied to rectify the problem, but ultimately we were unsuccessful under the given schedule due to facility access limitations. We were unable to decarbonate (charge) the system for more than a few minutes at a time, which was much shorter than the design target of 10 hrs.

A minor mechanical issue was that the vacuum pump deposited a green gelatin film inside the tubing down stream of the pump which was identified as the green glycol solution of the pump cooling system. This once fouled out a mass flow controller (which was repaired) and fouled out

the oxygen sensor which was intended to monitor for air ingress. The glycol presumable added moisture to the system which would have affected long term adsorption kinetics.

Task 2.6: Techno economic analysis of commercial plant

Collaboration with EPRI

A project feasibility-level financial analysis based was conducted using best estimates for the APOLLO system cost and performance. The levelized cost of electricity (LCOE) was the main financial metric in this analysis. The System Advisory Model (SAM) developed by the National Renewable Energy Laboratory (NREL) was selected as the financial model to determine the LCOE for the APOLLO project. In addition to the reference case, other work included sensitivity analyses on key project characteristics and their potential impact on the LCOE.

Subtask 2.6.1: TEA update – Sorbent Regeneration

Milestone 2.6.1: 30-year sorbent expenses

For the investigation of the optimal regeneration/replacement method to use to mitigate lifetime sorbent costs three separate techniques were considered that incorporate the sorbent degradation over time. The first two methods feature an annual regeneration, while the first method only has one complete swap out of sorbent, the second method has the sorbent swapped twice. The third method does not contain any regeneration steps, however, 10% of the sorbent is replaced with new sorbent every year. That equates to one 40-ton truck load every 22 days (Figure 25).

The sorbent degradation model uses a power decaying model that asymptotes towards a value that is approximately 2/3rds of the original capacity. The analysis used an initial sorbent capacity that was 0.40 gCO_2/g sorbent, however, due to the power function the capacity it had decayed by 11% in the first year for all cases (before any recover/replacement actions were taken). The regeneration with full replacement sees much greater variability between high capacity times and lower, while the replacement method reaches an equilibrium after about 5 years.

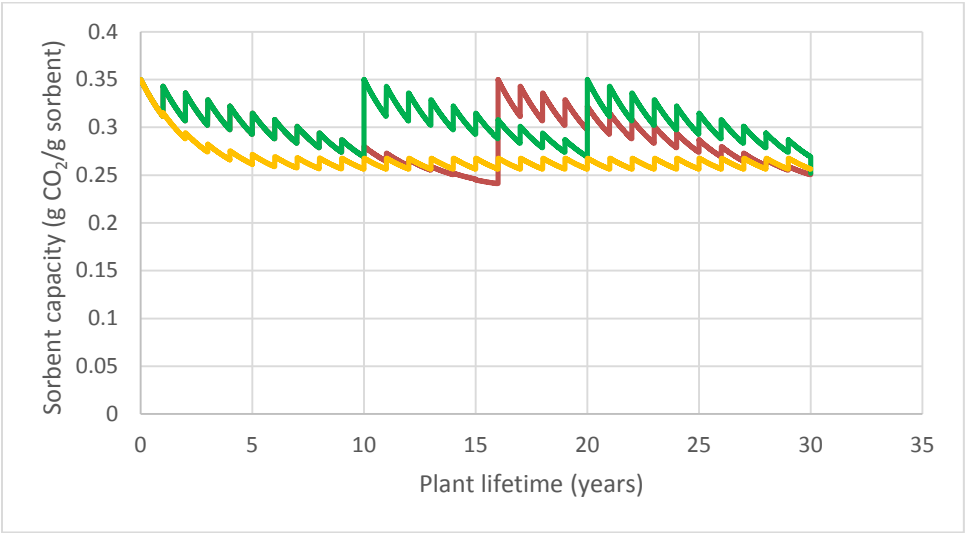


Figure 24. Sorbent Capacity Profiles for different Regeneration/Replacement Methods

The average sorbent capacity over the life of the plant is shown in *Table 5*. For calculating the required amount of "oversize" for the plant to accommodate some of the sorbent decay, one standard deviation of the sorbent capacity was subtracted from the average. It is assumed that the sorbent exchanges and regenerations would occur during an annual maintenance period not to exceed a few days.

Table5. Sorbent "oversizing" to accommodate sorbent decay.

	Average Sorbent Capacity (g/g)	Standard Deviation (g/g)	Lower Sorbent Capacity	Required Sorbent at Lower Capacity (tons)	Maximum Sorbent Price	Cost at $500/ton
10% Replacement per year	0.27	0.015	0.252	10,478	$572.66	$ 2.62
Single replacement with regeneration	0.29	0.026	0.263	13,403	$ 447.67	$ 3.35
Two replacements with regeneration	0.30	0.019	0.285	18,533	$ 323.75	$ 4.63

The findings show that while the replacement method, while maintain a lower average capacity, requires much less sorbent over the lifetime of the plant and allows for higher potential sorbent costs while still meeting the $3/kwh threshold. At the estimated $500/kg, two cases meet the

APOLLO targets and will be used for further analysis in Monte-Carlo simulations for plant performance.

Subtask 2.6.2: TEA update – Balance of Plant

Significant progress has been made in reducing the balance of plant component costs. The latest estimate for near-term system deployment cost is \$21.92/kWh$_{th}$, with pathways to further reduce cost to \$14.27/kWh$_{th}$, and \$10.90/kWh$_{th}$ in the future (*Table 6*, Figure 26).

Milestone 2.6.2

Cost estimates have been updated since phase I (Milestone 1.3.4 – Balance of Plant Cost) to reflect advancements in both system and component designs. These additional cost saving opportunities are possible through advancements in two key areas, gas storage, and maximum receiver temperature.

Using a high temperature receiver allows the CaO sorbent to decarbonate at much higher partial pressures, reducing the compression ratio between decarbonation and storage, and increases round-trip exergy efficiency. For T_equilbrium≥860°C (decarbonation equilibrium temperature) and with a $dT_{HTF\text{-}Sorbent} \leq 50°C$ the proposed system meets 95% target for round trip exergy efficiency.

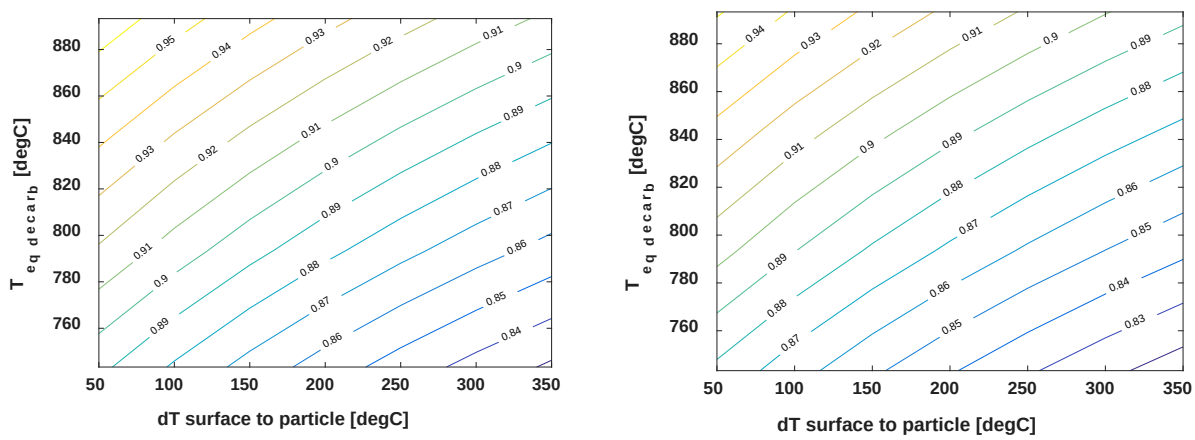


Figure 24: Round-trip exergy efficiencies of: a high temperature receiver with heat recovery turbine (a) vs. without turbine (b). Horizontal axis is the temperature difference between the HTF and the sorbent during decarbonation.

Working with Siemens, SR estimates that the higher operating pressure during decarbonation, and thus lower compression factor, will reduce the number of compressors stages from 3 to 1, at a cost savings of ~\$15 million compared to the system described in the Phase I continuation report. If higher receiver temperatures can be delivered the decarbonation process could happen

at atmospheric pressures and no compression would be needed at all, which would reduce total capital costs by an additional $5 million.

Table 6. BOP component costs for near-term and future system designs. Current near term systems with high temperature receivers achieve a total capital cost of $21.92/kWh$_{th}$.

	Near-term from continuation report	With near-term gas storage, with increased receiver temperature (T_eq>=820 degC)	Future low-cost, gas storage, with increased receiver temperature (T_eq>=820 degC)	Future low-cost, gas storage, very high receiver temperature (T_eq>=893 degC)
Low P HX Reactor, HPHX, Na pump	$11,767,584	$11,767,584	$11,767,584	$11,767,584
Compressor	$20,000,000	$5,000,000	$5,000,000	0
Gas Storage	$28,000,000	$14,600,000	$3,280,000	$3,280,000
Sensible Heat Storage	$1,100,000	$1,100,000	$1,100,000	$1,100,000
sub-total	$60,867,584	$32,467,584	$21,147,584	$16,147,584
Contingency, fees, etc. (+35%)	$21,303,654	$11,363,654	$7,401,654	$5,651,654
Total Capital Cost	$82,171,238	$43,831,238	$28,549,238	$21,799,238
Total Capital Cost $/kWh_th	$41.09	$21.92	$14.27	$10.90
LCOE_real ($/MWh)	$65.57	$59.08	$57.09	$56.31

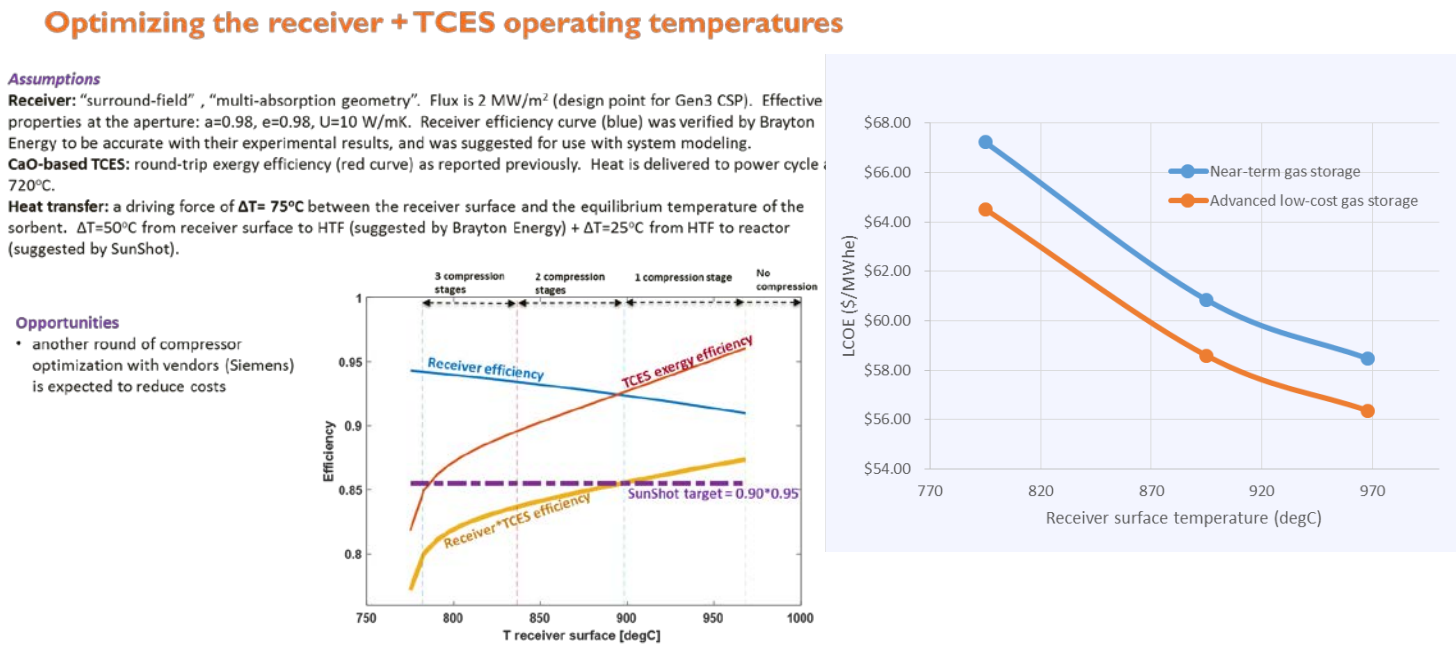


Figure 25. LCOE target (60 $/MWhe) is met or exceeded for the system with advanced low-cost gas storage with a receiver temperature ~870°C

Significant Accomplishments and Conclusions

The primary accomplishments under the ELEMENTS project focused on (1) the development and optimization of a high temperature, stable calcium oxide based sorbent for the storage of thermal energy, (2) the design of a viable high temperature thermal energy storage heat exchanger reactor, and (3) the evaluation of the system and its potential for commercialization based on system design and economic analysis. The following are primary achievements and associated conclusions developed under the APOLLO project, which focused on optimization and scaleup of the system:

- The thorough evaluation of potential sorbent types, characteristics, and compositions that lead to viable capacity targets as well as durability. The systematic evaluation of sorbents yielded a series of sorbents, with one specific formulation (recipe 5.5) that provided the best combination of capacity and durability.
- Production of the sorbent in a significant quantity (~30 kg) in a commercial viable co-precipitation process which obviates the need for a separate pelletization process. Pelletizing sorbent generally increases crush strength but decreases the hig-cycle durability of the sorbent.
- Development of multiple feasible heat exchanger reactor designs to meet performance targets and revision of reactor designs to meet cost targets. Shell and tube and printer

circuit heat exchanger designs are the primary viable targets, although costs remain high due to material requirements for sCO_2 cycle applications.

- Completion of integrated system design for commercial applications to meet system performance requirements and a path forward to potentially meet cost targets. The final system design uses a pure CO_2 system rather than a carrier gas and thus allows for less gas moving equipment, gas storage, and related balance of plant.
- Major developments in the TEA include 1) reduction of the cost of membrane gas storage for the near-term and future systems and 2) integration with liquid metal receivers for higher decarbonation temperatures and pressure will reduce the cost of gas compression and increase system efficiency. The result are three scenarios with costs bases of \$21.9, \$14.3, and \$10.9/kWh_{th} corresponding to a real LCOE of 59, 57, 56 \$/MWh_e, respectively.
- The prototype system heat exchange reactor has been designed with state-of-the-art modeling tools to ensure 1) sufficient thermo-mechanical lifetime of the Incoloy body and 2) performance of the packed bed reactor will be adequate to meet the milestones. The rest of the pilot system has been designed with off-the shelf components to maximize reliability and cost effectiveness. The system is highly instrumented including active thermal insulation, and a closed loop CO_2 circuit using a gas filled bladder with level measurement, for independent measurements of the heat and mass balances respectively.
- The 4 kWh prototype has 8 channels with commercially relevant geometry and a closed CO_2 system. The amount of sorbent has been scaled up by an impressive factor of 50.
- The basic operations of the energy storage system were demonstrated for carbonation (discharging) and decarbonation (charging) over short time periods. Excellent control of the CO_2 mass balance across the reactor was achieved with mass flow controllers and the basic operation of the level control of the CO_2 gas bladder was achieved. The system was apparently free from leaks and operated continuously for 18 days with no mechanical failures, thus meeting milestone 2.5.5. The major shortcomings of the system had to do with the controls which prevented us from deep cycling and or reaching high cycles. We were unable to decarbonate (charge) the system for more than a few minutes at a time, which was much shorter than the design target of 10 hrs.

Inventions, Patents, Publications, and Other Results

Currently, a single patent application has been filed to cover intellectual property associated with the integrated TCES system and reactor. The patent application was filed on June 15, 2016 with application number 15/183,101 with the title HIGH TEMPERATURE THERMOCHEMICAL ENERGY STORAGE SYSTEM, and inventors Santosh Gangwal, Ryan Melsert, and Tim Hansen. The patent is pending at time of this report

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