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EXECUTIVE SUMMARY

Southern Research has developed a thermochemical energy storage (TCES) technology that utilizes the endothermic-exothermic reversible carbonation of calcium oxide (lime) to store thermal energy at high-temperatures, such as those achieved by next generation concentrating solar power (CSP) facilities. The major challenges addressed in the development of this system include refining a high capacity, yet durable sorbent material and designing a low thermal resistance low-cost heat exchanger reactor system to move heat between the sorbent and a heat transfer fluid under conditions relevant for CSP operation (e.g., energy density, reaction kinetics, heat flow).

The proprietary stabilized sorbent was developed by Precision Combustion, Inc. (PCI). A factorial matrix of sorbent compositions covering the design space was tested using accelerated high throughput screening in a thermo-gravimetric analyzer. Several promising formulations were selected for more thorough evaluation and one formulation with high capacity (0.38 g CO_2/g sorbent) and durability (>99.7% capacity retention over 100 cycles) was chosen as a basis for further development of the energy storage reactor system.

In parallel with this effort, a full range of currently available commercial and developmental heat exchange reactor systems and sorbent loading methods were examined through literature research and contacts with commercial vendors. Process models were developed to examine if a heat exchange reactor system and balance of plant can meet required TCES performance and cost targets, optimizing tradeoffs between thermal performance, exergetic efficiency, and cost. Reactor types evaluated included many forms, from microchannel reactor, to diffusion bonded heat exchanger, to shell and tube heat exchangers. The most viable design for application to a supercritical CO_2 power cycle operating at 200-300 bar pressure and >700°C was determined to be a combination of a diffusion bonded heat exchanger with a shell and tube reactor.

A bench scale reactor system was then designed and constructed to test sorbent performance under more commercially relevant conditions. This system utilizes a tube-in tube reactor design containing approximately 250 grams sorbent and is able to operate under a wide range of temperature, pressure and flow conditions as needed to explore system performance under a variety of operating conditions. A variety of sorbent loading methods may be tested using the reactor design. Initial bench test results over 25 cycles showed very high sorbent stability (>99%) and sufficient capacity (>0.28 g CO_2/g sorbent) for an economical commercial-scale system.

Initial technoeconomic evaluation of the proposed storage system show that the sorbent cost should not have a significant impact on overall system cost, and that the largest cost impacts come from the heat exchanger reactor and balance of plant equipment, including compressors and gas storage, due to the high temperatures for sCO_2 cycles. Current estimated system costs are \$47/kWh_{th} based on current material and equipment cost estimates.

TABLE OF CONTENTS

EXECUTIVE SUMMARY 2
Background 4
Project Objectives 10
Project Results and Discussion 11
1.0 Budget Period 1 11
1.1 Sorbent Material Refinement 12
1.1.1 Baseline Sorbent Performance 14
1.1.2 Sorbent Optimization 15
1.1.3 Chemical and Physical Characterization 17
1.1.4 Three Sorbent Downselect, 100-Cycle testing 18
1.1.5 Sorbent Pelletization 19
1.1.6 1,000 Cycle Pelletized Sorbent Testing 24
1.2 Reactor Design, Modeling, and Simulation 25
1.2.1 Chemical Kinetic Modeling 25
1.2.2 Optimize HTF Tube-side Sizing and Geometry 27
1.3 HxRx Reactor Design 29
1.3.1 HxRx Requirements and Specification 30
1.3.2 Bench Reactor Design, Construction and Commissioning 33
1.3.3 Sorbent Loading Methods 36
1.3.4 Bench Scale Tests, milestones 2.1.3, 2.1.4 37
1.4 Technology Transfer Package 39
1.4.1 Reactor and Balance of Plant Cost 40
Significant Accomplishments and Conclusions 44
Inventions, Patents, Publications, and Other Results 45
Path Forward 45
References 47

Regenerative Carbonate-Based Thermochemical Energy Storage System for Concentrating Solar Power

Background

Recently, calcium oxide (CaO)-based sorbents have been developed primarily for application to CO_2 capture from fossil fuel power plant gases followed by production of a concentrated (>95 volume % CO_2) sequestration-ready CO_2 stream. Most recent studies have concentrated on developing a sorbent and a CO_2 capture process using the sorbent for preparing a concentrated CO_2 stream. This has dictated that $CaCO_3$ decomposition (regeneration) occurs in the presence of a nearly pure CO_2 environment and this in turn requires the use of 900ºC or higher temperature for regeneration to overcome thermodynamic equilibrium limitations. However, based on our review of literature studies and further corroboration from our experiments, the 900ºC regeneration appears to be a major cause of degradation of synthetically prepared CaO sorbents, most likely due to sintering of the $CaCO_3$/CaO particles. Only a few studies have been found in the literature that have evaluated the use of the CaO-CO_2 reaction for energy storage, or for a chemical heat pump, as opposed to CO_2 capture/sequestration.

Literature Studies Specific to Energy Storage rather than CO_2 Capture

Beginning with a paper by Barker (1974), only a few papers (Kyaw et al., 1996a, 1996b; Aihara et al., 2001) have actually appeared in the literature on the use of CaO-based sorbents specifically for energy storage rather than CO_2 capture. Barker (1974), employing nano-particles of $CaCO_3$, demonstrated the need for pressing/pelletization to increase density both for practical use in a reactor as well as to increase volumetric energy density of the TCES reactor.

Aihara et al. (2001) attempted to stabilize calcium oxide with calcium titanate ($CaTiO_3$) using two methods: (1) Alkoxide method starting with Ca metal, ethanol, and titanium tetra isopropoxide to form calcium oxide and calcium titanate in-situ during calcination and (2) physically mixing $CaCO_3$ and $CaTiO_3$ in ethanol followed by calcination. A sample was also made just using $CaCO_3$. Carbonation using 20 % CO_2/N_2 and calcination using pure N_2 were conducted isothermally at 750ºC (1023 K) for 1 hour each for 10 cycles on each sorbent. The sample made just with $CaCO_3$ showed nearly a 50 % drop in capacity starting with 67 % conversion, whereas the other two made with $CaTiO_3$ showed stable conversion at 61 %. Also, the surface area of the $CaTiO_3$ containing sorbents was stable over the 10 cycles, whereas that of the $CaCO_3$ only sorbent dropped by nearly 45 %.

The authors claim that calcium titanate prevented the sintering of the reactive particles of CaO and stabilized the reversibility of the reaction. Onset of sintering can occur at T_T, which is about ½ melting temperature. The melting point of CaO is 2200 K, that of $CaTiO_3$ is 2840 K, but that of $CaCO_3$ is 1600 K. Although at 1023 K, sintering of formed $CaCO_3$ can occur, it was apparently prevented by the presence of $CaTiO_3$. Although many more cycles need to be run on these materials before they can be proven successful, it is instructive to note that the calcination temperature used was 750ºC

rather than 900ºC (as typically used for CO_2 capture sorbents), and this probably contributed to the stability of the titanate containing sorbents. On the other hand, the $CaCO_3$-only sorbent degraded even at this lower temperature.

Literature Studies on Sorbent Development for CO_2 Capture

A detailed and excellent review has been recently published on development of CaO-based CO_2 sorbents (Kierzkowska et al., 2013). Summarized below are some important observations from this review:

- CaO derived from limestone shows a rapid cycle to cycle decrease in its capability to capture CO_2 presumably due to reduction in available pore volume with cycles.
- Carbonation occurs in two stages—a rapid first kinetics-controlled stage followed by a very slow diffusion controlled second stage
  - Through simplistic CO_2 diffusivity calculations based on data, Barker (1973) proposed a critical thickness of 22 nm for $CaCO_3$ product layer above which the reaction becomes diffusion limited.
  - Bhatia and Perlmutter (1983) proposed that the rapid stage is governed by the filling of the small pores (40-150 nm) and then substantially slower reaction continues in the larger low surface area pores. From the very low estimated diffusivities, these authors theorize that the slow reaction stage is actually governed by solid-state diffusion.
- Our TGA results corroborate that carbonation may be a two-step process, with a relatively sharp shift from the rapid Stage 1 to the slow Stage 2. On the other hand, regeneration (or calcination or decarbonation) appears to be a single step process. These results are corroborated by past studies described in the literature.
- A simple explanation is that the mechanism during carbonation rather sharply changes from that of reaction rate control to both reaction and product layer diffusion rate control (Grasa et al., 2009). A deeper answer per Bhatia and Perlmutter (1983) is closure of small pores followed by continuation of the reaction at a much slower rate due to larger pores. We interpret this to mean that the sorbent particle contains small grains as well as large grains, with the smaller grains reacting quickly during reaction rate control stage followed by the closure of the path leading to them due to larger $CaCO_3$ molecule compared to CaO. A very thin product layer on the order of 30 nm around the small grains is apparently sufficient to make CO_2 diffusion to them extremely slow. On the other hand, during regeneration, CO_2 is evolving and diffusing to the outside rather than diffusing to the inside of the particle or the individual grains. Thus after an extremely short, perhaps negligible in terms of time, period of relatively slow evolution, sufficient porosity is created for CO_2 to begin quickly diffusing out from the inside through the porous CaO layer, thus giving the results the appearance of a single step.
- The main strategy proposed to overcome limestone's limitations has been the development of synthetic CaO-based sorbents. Although hydration and thermal treatment have also been proposed as alternative strategies, in our opinion, these strategies are less likely to be applied due to cost and technical issues.
- For preparation of synthetic sorbents, the following methods have been mainly employed:

- Calcination of synthetic CaO precursors to achieve high surface area and pore volume
- Hydrothermal synthesis using CaO precursors
- Stabilizing CaO with high Tammann temperature (T_T) supports
- Supports forming mixed oxides with CaO, for example Al_2O_3 that forms mayenite ($Ca_{12}Al_{14}O_{33}$)
- Supports not forming mixed oxide with CaO for example MgO
- Supports that are themselves CO_2-active
- Preparation of nano-sized CaO particles for example using sol-gel techniques
- Doping of CaO for example using alkali metals to reduce the regeneration temperature

Use of supports that do form mixed oxides such as mayenite appear to be the most successful method of making stable sorbents. The best stabilizer appears to be alumina and studies based on alumina are discussed further below.

CaO Sorbents Stabilized Using Alumina to Form Mayenite

A number of approaches have been used to produce synthetic CaO sorbents stabilized with alumina (Li et al., 2005; Wu et al., 2008; Martavaltzi and Lemonidou, 2008; Dennis and Pacciani, 2009; Broda et al, 2012 a, 2012b; Manovic and Anthony, 2009; Manovic and Anthony, 2010; Kazi et al., 2014). In all these studies, formation of mayenite during high temperature calcination has been credited for contributing to the stability. Except for Manovic and Anthony, who have used naturally occurring limestone, investigators have used reagent grade starting materials in their preparations.

Wu et al. claimed that formation of mayenite stabilized the nanostructured morphology of their sorbent. However, their sorbent contained only 35 wt % CaO and thus had low capacity. Recent results of Kazi et al. confirm the Wu et al. results. Broda et al combined sol-gel with alumina stabilization to prepare their sorbents. The sizes of CaO nano-particles in their sorbent were in the 100-250 nm range. Their best sorbent contained 91 % CaO and captured 0.51 g CO_2 per g sorbent consistently over 30 cycles at 750°C isothermal operation. However, when the calcination temperature was increased to 900°C, the capacity dropped precipitously to 0.28 g/g after just 10 cycles. This result provides further evidence that 900°C calcination is simply too severe and degrades the sorbent by potentially sintering of the low T_T $CaCO_3$ particles even with mayenite stabilization.

Broda and Muller (2012) further improved Broda et al.'s sorbent's capacity to a constant 0.56 g CO_2/g sorbent (750°C isothermal operation over 30 cycles) by incorporation and removal of a carbon template in the sorbent to form hollow microspheres with a grain size of 170 nm. Addition of alumina to form mayenite was a necessary step that imparted stability.

In a very recent paper (Angeli et al. 2014), stabilization of a sol-gel preparation using a calcium aluminum-oxygen phase ($Ca_3Al_2O_6$) different from mayenite was claimed. However, the calcinations were performed at 800°C by Angeli et al. as opposed to 750°C, so it is difficult to make a direct comparison of this sorbent with Broda's mayenite-stabilized sorbent. Sorbents made by sol-gel without alumina stabilization

performed poorly (Santos et al, 2012), which lends credence to the necessity of alumina stabilization via mayenite formation.

In contrast to investigators mentioned above, Manovic and Anthony (2009a, 2010) have taken a different route. They have proposed the use of inexpensive naturally occurring starting materials for CaO rather than reagent grade materials, along with commercially available calcium aluminate cement as a binder to make pellets. In their study of binders in the sorbent ranging in concentrations from 5 to 40 %, they have shown that calcium aluminate at a level of 10 wt % has the best performance. They used 90 % CaO and 10 % calcium aluminate containing about 75 % alumina to make the sorbent. They further claim that calcination led to the formation of mayenite in their sorbent as well, with alumina coming from the binder and calcium coming both from the binder and from CaO. The final composition of their sorbent is claimed to be about 80% CaO and 20 % mayenite. These sorbents degrade like others when using a calcination temperature of 900°C. However with isothermal operation at 750°C, the activity stabilized at 67% conversion over 30 cycles after some initial deactivation. These authors claim that their sorbents are better suited commercially because of the low cost of starting materials and the simplicity of their preparation method leading to pellets.

Pelletizing

Manovic and Anthony (2009 b) used naturally occurring limestone to make their sorbents. According to their paper, both reactivation of spent sorbent and preparation of modified CaO-based sorbent may be required to maximize the performance of their sorbent. However, one of their methods to achieve reactivation, namely, hydration, seems to weaken the particles. Thus, it is expected that pelletization of the obtained powder may be required. Manovic and Anthony have screened two bentonites (Na- and Ca-bentonite) and four types of commercial calcium aluminate cements (CA-14, CA-25, Secar 51, and Secar 80), with a primary focus of maintaining a high CO_2-capture capacity over 30-35 cycles. The tests were carried out using a TGA, and the results showed that the presence of bentonites led to faster decay in activity as a result of the formation of calcium-silica compounds with low melting points, which lead to enhanced sintering. This was confirmed by scanning electron microscopy (SEM) and also X-ray diffraction (XRD), which showed the presence of spurrite [$Ca_5(SiO_4)_2CO_3$] as the dominant compound in the pellet after this series of cycles. Better results were obtained with no binder, i.e., by hydration of lime, where $Ca(OH)_2$ played the role of the binder. Promising results were obtained also with calcium aluminate cements, as, unlike bentonites, the presence of these binders did not cause sintering. These results with calcium aluminate cements are particularly promising for practical application because these cements have a number of very favorable properties, such as fast setting and good refractory properties, and finally, they are inexpensive and easily obtained commercially in large quantities. Thus, on the basis of this study, pelletization without a binder, or pelletization using about 10 wt% use of calcium aluminate cements, appear to be the pelletization routes that should be pursued.

Recently, Kazi et al. investigated the influence of mayenite content on the strength of synthetic CaO sorbent particles and compared it to naturally occurring limestone. The limestone particles were significantly weaker after calcination. All mayenite containing sorbents showed a higher crushing strength than the calcined sorbent. Also, increasing

the mayenite content increased the crushing strength of the synthetic sorbents particles from 1.7 N with 27 % mayenite to 5.4 N at 73% mayenite.

Kinetic Modeling of CaO-CO_2 Reaction

Earlier studies by researchers on lime carbonation actually indicated a relatively rapid initial reaction rate followed by a much slower second stage around 60 to 70 % CaO conversion [Bhatia and Perlmutter, 1983; Barker, 1973,1974]. Synthetic sorbents with meso-pores can reach 90+ % CaO conversion before entering the second slow reaction stage as indicated by later studies [Gupta and Fan 2002; Fan et al, 2013]. Bhatia and Perlmutter (1983) have attributed the sudden slowdown in the second stage to closure of small pores followed by continuation of the reaction at a much slower rate due to larger pores. We interpret this to mean that the sorbent particle contains small grains as well as large grains, with the smaller grains reacting quickly followed by the closure of the path leading to them due to the larger $CaCO_3$ molecule compared to CaO.

Bhatia and Perlmutter (1983) pioneered the development of the random pore model to describe their experimental TGA lime carbonation results for various limes prepared by calcining naturally occurring limestones. Their model is highly informative for understanding by what structural parameters the rate of CaO-carbonation reaction is determined. It however is somewhat complex to employ.

Grasa et al. (2009) have developed a somewhat simplified version of the random pore model. The carbonation reaction was successfully described as a two stage reaction. In the first stage, the carbonation was controlled by chemical reaction and in the second period there was combined control by chemical reaction and CO_2 diffusion through the product layer. The model was applied to determine the thickness of the product layer that marked the change in the reaction mechanism. This was found to be around 30–42 nm for the limestones tested for different conditions and cycle numbers, with a mean value of 38 nm.

Lee (2004) argued that from a practical point of view, instead of a complex random pore model, a kinetic equation with the best fit to experimental conversion data could be very useful for process design. The literature-reported carbonation conversion behavior of two CaO samples [Gupta and Fan, 2002; Bhatia and Perlmutter, 1983] at various temperatures above 550°C was shown to be well represented with the simple apparent conversion-time equation:

$$X = kbt/(b + t)$$

Where X = conversion, k = rate constant (1/sec), b is the time in seconds for 50 % conversion, and t is time (sec).

Temperature dependencies of parameters *k* and *b* were determined in the form of Arrhenius equation for the carbonation reaction in the two control regimes, respectively. The activation energy in the carbonation of surface CaO with CO_2 was estimated to be about 72 kJ/mol regardless of the source of CaO, however, that in the diffusion control regime appeared differently as 102.5 for a mesoporous CaO [Gupta and Fan, 2002] or 189.3 kJ/mol for commercially available CaO [Bhatia and Perlmutter, 1983], possibly due to the morphological differences of the two CaO samples. The proposed model

equation deserves attention in that the CaO-carbonation behavior at temperatures higher than 700 ◦C for maximizing CaO conversion could be closely predicted.

Finally, Liu et al. [2012] developed their version of the grain model (so called overlapping grain model) using TGA and fluidized-bed reactor data to describe the kinetic behavior of a sorbent that was similar to the ones being studied in this project in that it contained mayenite. In-situ XRD investigations by Liu et al. verified the inertness of mayenite in their synthetic sorbent. The mayenite neither interacted with the active CaO nor did it significantly alter the carbonation–calcination equilibrium. For the model, the microstructure of the sorbent was defined by a discretized grain size distribution, assuming spherical grains and a single value of the diffusivity of CO_2 in the growing layer of product $CaCO_3$. The distribution was used as an input parameter to the model to predict the rate and extent of CO_2 uptake by the sorbent. The complex nature of the actual microstructure of the solid posed some difficulty in obtaining the grain size distribution directly from porosimetry measurements. Nonetheless, the model was able to predict the performance of the material well and, particularly, was able to account for changes in rate and extent of reaction as the structure evolved after various numbers of cycles of calcination and carbonation.

Based on this review and further analysis of our empirical TGA data, we have developed a kinetic model to be used in our multi-physics FEA reactor model being developed in this project. We will also review the kinetic models available for regeneration (a simpler phenomenon compared to carbonation) and select a suitable model for input into the FEA reactor model.

Summary Takeaways from the Literature Review

- Review of several papers consistently suggests that 900°C regeneration temperature leads to degradation of CaO sorbent capacity, presumably due to sintering of calcium carbonate particles. In contrast, regeneration at 750°C appears to yield high sorbent stability in studies by some researchers, which is confirmed by our empirically collected TGA scale data
- Reduction of the regeneration temperature to 750°C with regeneration using a low concentration CO_2 stream is feasible for TCES application, but not for CO_2 capture/sequestration applications
- At lower regeneration temperatures, a higher CaO content can be used as we and others have demonstrated. However, at regeneration temperatures of 900°C, 37 wt % CaO (with a CO_2 capacity of 0.3 g CO_2/g sorbent) appears to be the limit
- Mayenite, or another stabilizer, is a necessary ingredient to circumvent the degradation during carbonation at 750°C as will occur in natural lime, irrespective of the preparation method used
- Increasing the CaO content to increase CO_2 capacity up to 0.5-0.6 g/g and maintain stability is feasible based on the work of Broda et al. if milder carbonation and regeneration temperatures are used
- Preparation using naturally occurring hydrated lime along with calcium aluminate cement could also be considered to reduce cost based on results by Manovic and Anthony

- Preferred method of pelletizing could involve either no binder (just moisture) or about 10 wt % commercial calcium aluminate binder, such as those used by Manovic and Anthony. The use of acidic binders tends to degrade the sorbent.

Project Objectives

The reversible carbonation of lime (CaO) is a desirable reaction for use in high-temperature thermochemical storage systems due to high heat of reaction and low material cost. There are two primary limitations that have historically mitigated performance and subsequent commercialization. The first limitation is the low durability of untreated lime, as macro-scale agglomerations and micro-scale pore closures dramatically reduce CO_2 uptake capacity over a short number of carbonation-decarbonation cycles. The second limitation of the system is the poor heat transfer between the solid sorbent and the high-temperature heat transfer fluid (HTF) which necessitates a large amount of surface area.

The first phase of the project addressed the sorbent durability challenges. Through previous work in refining calcium-based sorbents for coal-fired flue gas CO_2 capture by project partner Precision Combustion Inc. (PCI), and review of the literature, it has been seen that reinforcing the calcium-oxide structure with PCI's sorbent stabilization process has a positive influence on sorbent durability. Through refining the sorbent material composition and preparation method, as well as optimizing and controlling the operating conditions during sorbent carbonation-decarbonation, the current work demonstrated that a high and stable CO_2 uptake capacity can potentially be achieved throughout the life of the sorbent. Promising sorbent materials were successfully identified at the laboratory scale in Phase 1. The Phase 1 go/no go decision point was met by identifying sorbent formulations meeting capacity (>0.36 g/g) and durability (> 0.995) metrics.

In Phase 2, heat exchange reactor designs were further developed and the selected sorbent was tested under commercially relevant conditions in a bench scale (~250 g sorbent) tube-in-tube reactor using pressure swing - as opposed to concentration swing - to control reaction direction and rate and with an HTF employed to deliver and remove heat. The second phase also addressed the design of a low thermal resistance and low cost heat exchanger reactor. The low thermal conductivity of the solid sorbent and the multi-step transfer of this heat to the HTF results in a large effective thermal resistance and a subsequent required large thermal gradient between the sorbent in the HTF. This requires large temperature swings to enable cycling, and for the exothermic carbonation to occur at a prohibitively high temperature to transfer heat to the HTF. The project addressed these challenges through innovative heat exchanger design, implementation of multi-mode heat transfer, and rigorous multi-physics simulation of the chemical kinetics, heat transfer, fluid dynamics, and structural mechanics of the system in an integrated environment.

Project Results and Discussion

1.0 Budget Period 1

A summary of all proposed milestones and associated results is provided in Table 1

Table 1. Budget Period 1 Milestone Summary Table

Milestone	Description	Success Value	Measured Value	Assessment Tool	Goal Met (Y/N)	Notes
Milestone 1.1.1	Demonstrate durability of 3 powder sorbent materials in TGA scale testing	> 0.9950	Sorbent 1-1 Run 1: 0.9952 +/- 0.0001 Run 2: 0.9951 +/- 0.0001 Run 3: 0.9967 +/- 0.0001 Sorbent 1-4 Run 1: 0.9954 +/- 0.0001 Run 2: 0.9954 +/- 0.0001 Sorbent 2-1 Run 1: 0.9986 +/- 0.0001 Run 2: 0.9990 +/- 0.0001 Run 3: 0.9968 +/- 0.0001	One-tailed t-test, 95% CI Data from TGA	**Yes** **(2 materials, 3rd test aborted on sorbent 1-4 due to capacity decline)**	
Milestone 1.1.2	Demonstrate capacity of 3 powder sorbent materials in TGA scale testing	> 0.38	Sorbent 1-1 Run 1: 0.4076 +/- 0.0001 Run 2: 0.4079 +/- 0.0001 Run 3: 0.4057 +/- 0.0001 Sorbent 1-4 Run 1: 0.3959 +/- 0.0001 Run 2: 0.3956 +/- 0.0001 Sorbent 2-1 Run 1: 0.3818 +/- 0.0001 Run 2: 0.3803 +/- 0.0001 Run 3: 0.3810 +/- 0.0001	One-tailed t-test, 95% CI Data from TGA	**Yes** **(2 materials, 3rd test aborted on sorbent 1-4 due to capacity decline)**	
Milestone 1.1.3	Demonstrate durability of 1 pelletized sorbent material in TGA scale testing	> 0.9500	NA	One-tailed t-test, 95% CI Data from TGA	**No**	Pelletized sorbent testing in TGA was determined to be a non-representative test method. Decision made to focus on pellet testing in fixed bed in bench reactor.
Milestone 1.1.4	Demonstrate capacity of 1 pelletized sorbent material in TGA scale testing	> 0.36	NA	One-tailed t-test, 95% CI Data from TGA	**No**	See Milestone 1.1.3

<table>
<tr><th>Milestone</th><th>Description</th><th>Success Value</th><th>Measured Value</th><th>Assessment Tool</th><th>Goal Met (Y/N)</th><th>Notes</th></tr>
<tr><td>Milestone 1.1.5</td><td>Demonstrate consistent CO2 absorption profile in carbonation cycle throughout 1,000 cycle pelletized sorbent TGA testing</td><td>95%</td><td>
<table>
<tr><th></th><th colspan="2">dw/dt_{fresh}: dw/dt_{aged}</th></tr>
<tr><th>fraction of wt gain of last cycle (%)</th><th>carb</th><th>decarb</th></tr>
<tr><td>0.7</td><td>0.86</td><td>1.00</td></tr>
<tr><td>25</td><td>0.82</td><td>0.95</td></tr>
<tr><td>50</td><td>0.73</td><td>0.89</td></tr>
<tr><td>75</td><td>0.56</td><td>0.79</td></tr>
<tr><td>90</td><td>0.27</td><td>0.54</td></tr>
</table>
</td><td>One-tailed t-test, 95% CI
Data from TGA</td><td>No
Achieved with 100 cycle powder tests</td><td>See Milestone 1.1.3</td></tr>
<tr><td>Milestone 1.1.6</td><td>Sorbent volumetric energy density (MJ/m3)</td><td>4,000</td><td>NA</td><td>Sensitivity Analysis</td><td>No</td><td>See Milestone 2.1.5</td></tr>
</table>

1.1 Sorbent Material Refinement

The reversible carbonation of lime is an attractive reaction for high-temperature thermochemical storage as it exhibits a high heat of reaction (~180 KJ/mol), a high theoretical absorption capacity (44g CO2 / 56g CaO, ~0.79 g/g), very few side reactions, and is a very low cost and abundant material. However, as described above, the sorbent undergoes rapid degradation of CO_2 uptake capacity when in its raw form.

To quantify the high capacity yet low durability of raw untreated limestone, a TGA experiment was performed using a TA Instruments Q600 SDT simultaneous thermogravimetric analyzer and differential scanning calorimeter (TGA/DSC). Approximately 25mg of raw limestone was cycled 10 times by decarbonating for 30min at 900C under 130 ml/min of pure N_2 and then carbonating for 30min at 750C under 130ml/min of 20% CO_2 in N_2. The initial CO_2 uptake capacity was indeed very high (0.77 g/g), however after 10 cycles the sorbent had degraded and the capacity fell to 0.21 g/g (Figure 1). This severe degradation over such a short number of cycles would lead to a thermochemical storage system that is not functionally or economically feasible for commercial operation.

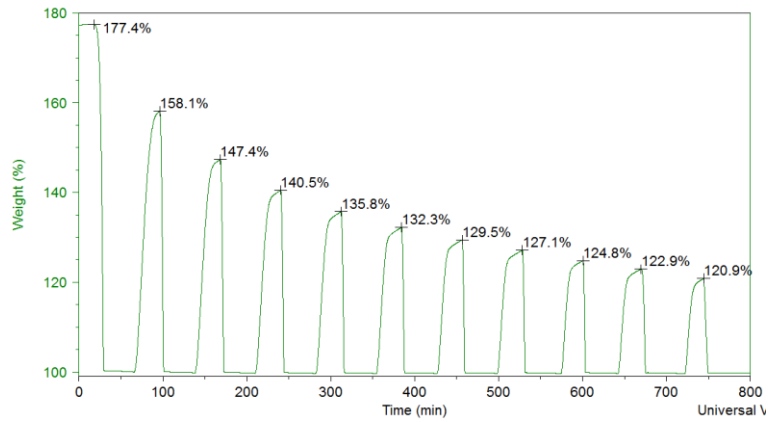


Figure 1: TGA results of cycling of raw untreated limestone

Investigation of the reaction kinetics from these experimental results shows that the carbonation of the calcium oxide sorbent occurs in two distinct stages, and the decarbonation occurs in a single stage (Figure 2). Each of these three stages are highly linear, and sharp changes in rate of absorption/desorption occur at the interfaces.

These stages are characterized by an initial rapid carbonation reaction whereas the surface of the sorbent is reacted with CO_2 to form a low porosity crust, and a much slower second stage carbonation which is limited by solid state mass diffusion as the CO_2 is forced to diffuse through the low porosity crust layer to access the unreacted calcium oxide core of the material. During decarbonation, only a single rapid reaction regime is experienced.

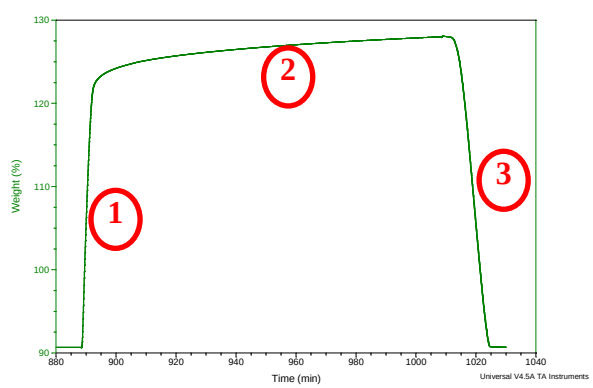


Figure 2: Example of 3-stage reversible carbonation/decarbonation cycle; Stage 1 shows rapid kinetically-controlled carbonation, stage 2 gas diffusion controlled carbonation, stage 3 rapid decarbonation

The posited explanation for this asymmetric reversible reaction is that during the carbonation phase the surface crust layer forms first, slowing down subsequent reactions by requiring additional CO_2 to permeate through this low permeability material. However, during decarbonation this surface crust layer is also the first to react and release CO_2, leaving behind a much higher porosity surface layer through which the CO_2 leaving the core of the particle can easily pass (Figure 3).

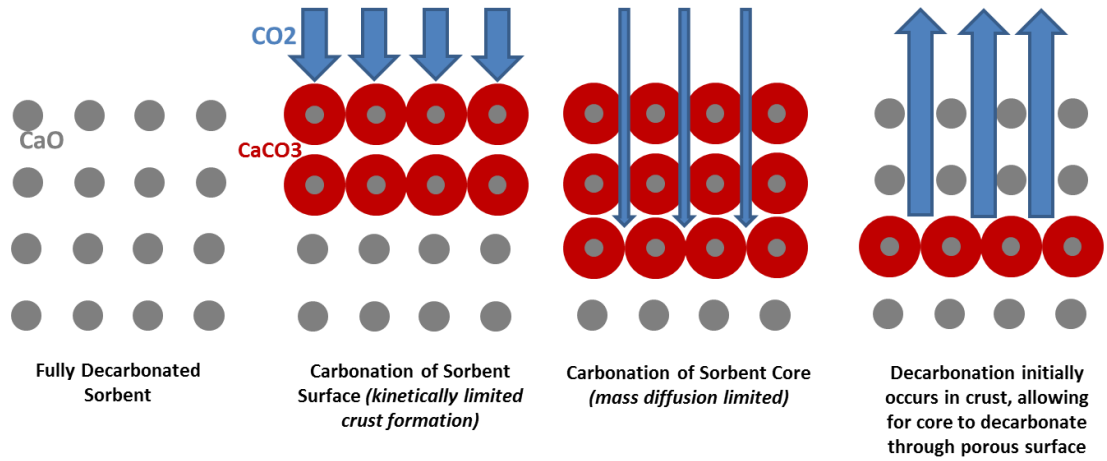


***Figure 3**: Illustration of reversible, yet asymmetric, calcium oxide carbonation/decarbonation reactions*

1.1.1 Baseline Sorbent Performance

Beyond use for high-temperature thermochemical storage, the reversible carbonation of lime is also being investigated for the capture of CO_2 in flue gas of coal fired power plants. While the desired attributes of an ideal sorbent are different in this application, the methods used to increase the durability of the limestone are transferrable. Project partner PCI has previously developed a CaO-based sorbent for CO_2 capture applications that has exhibited significant increases in durability under flue gas conditions. This PCI developed sorbent was used as the baseline refined sorbent in the current work, and its capacity and durability were quantified under storage system relevant conditions.

In CO_2 capture application testing (carbonation at 750°C for 1hr under 20% CO2, decarbonation at 900°C for 1hr under pure N_2), PCI previously demonstrated a sorbent capacity of 0.30 g/g and near zero degradation of capacity over 45 cycles.

The baseline PCI sorbent was first tested by carbonation at 750°C under 20% CO_2 for 1hr and decarbonating at 750°C under pure N_2 for 1hr. The results (Figure 4, left) show an initial low uptake of CO_2 that gradually increased, and after 100 cycles 0.32 g/g were being absorbed. This activation period as uptake capacity was gradually increased is attributed to the structuring of the surface morphology of the sorbent and increased access to the pore structure. While the final capacity is attractive, and there is no degradation of capacity over the experiment, an activation period of 100 cycles (equal to 100 days in CSP applications) is not feasible.

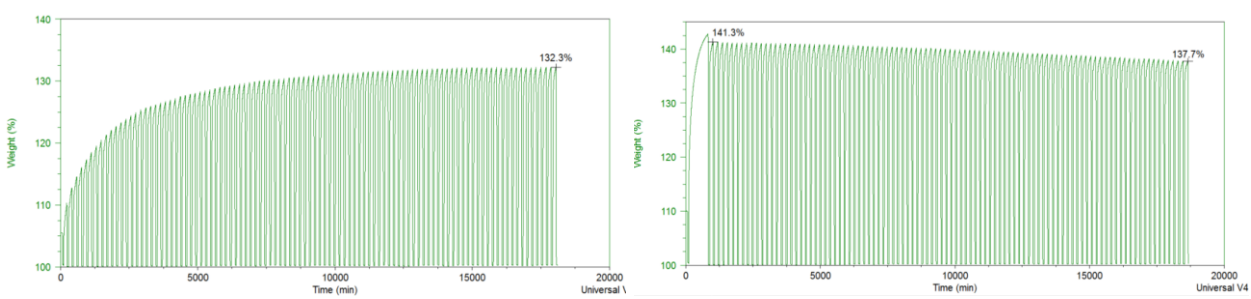


Figure 4: TGA cycling of PCI baseline material (left) without activation, (right) with activation

A subsequent TGA test was performed on the same PCI baseline material under the same cycling conditions, however, an activation period was added to the start of the run. After drying at 125°C for 30min, the material was calcined at 900°C for 10min to drive off volatiles, and then the material was held in a single continuous carbonation phase for 12hr while the micro-pores structured, and then the material was cycled as in the first run. The hypothesis was that by allowing the material to structure in a single extended activation period, the subsequent cycling would occur at full capacity. The results from this run (Figure 4, right) showed a highly activated material in the first cycle with a capacity of 0.41 g/g. However, the sorbent capacity decreased to 0.38 g/g over 100 cycles in a near linear fashion.

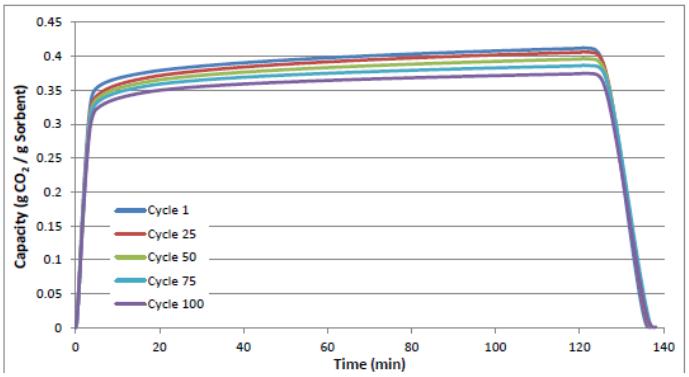


Figure 5: Absorption/desorption profile of PCI baseline material over 100 cycles

1.1.2 Sorbent Optimization

<u>Composition Matrix</u>

In order to examine the impact of material composition on sorbent capacity and durability, a test matrix was developed to prepare and test additional sorbent samples. A total of 12 samples were prepared, having varying weight ratios of CaO and proprietary stabilizing components.. These ratios result in samples that have higher and lower stabilizer content than the baseline material, allowing for relationships to be developed between sorbent composition and capacity/durability.

Figure 6: Test matrix of sorbent material compositions (redacted)

The quantitative material compositions that result from these ratios for the 12 samples are proprietary and not revealed here. Sample 1-0 is the PCI baseline material, and the other 11 samples were selected to fully explore the design space and quantify the impacts of material composition of sorbent capacity and durability.

Table 2: Composition of test samples (redacted)

Table 3: Composition of test samples (redacted)

Figure 7: Maximum theoretical capacity of each sample material (redacted)

High Throughput Screening

The goal of the screening process is to develop relationships between sample composition and sorbent capacity and durability. Each sample was tested under accelerated conditions to minimize overall testing time and resources. The test procedure consists of sample drying for 30min at 125°C, calcining for 10min at 900°C, activation at 750°C for 1hr under 25% CO_2, and then 25-50 alternating cycles of decarbonation at 750°C under pure N_2 for 30min and carbonation at 750°C under 20% CO_2 for 1hr. Each of these accelerated tests requires ~3 days, and each sample was tested twice. The general trends of these results are shown in Figure 8, and the quantitative sorbent capacities and sorbent durabilities are shown in Figure 9.

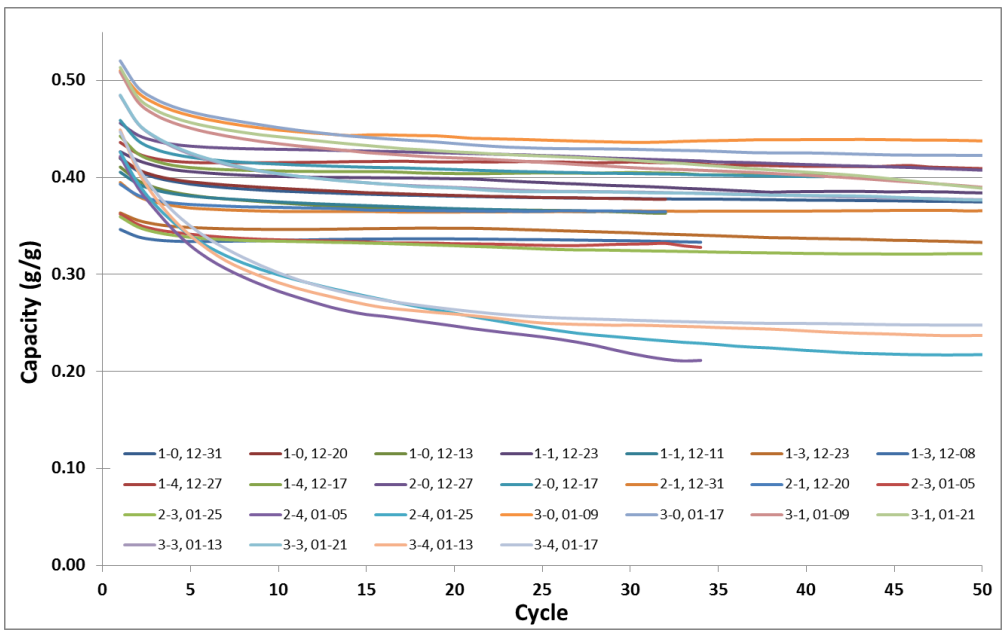


Figure 8: Capacity vs. cycle trendlines of HTS results

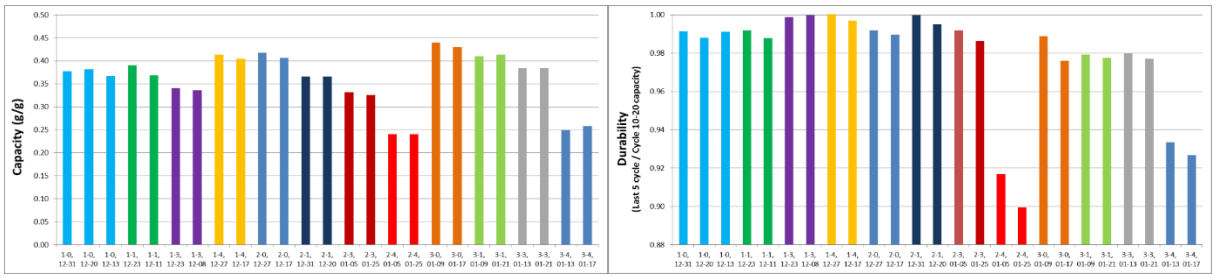


Figure 9: Sorbent capacity and durability results of HTS testing

The screening results show wide ranging capacity and durability performance. Many of the medium CaO sorbents (2-X) show higher CO_2 capacity than the low CaO materials (1-X) with minimal impact on durability, however the high CaO sorbents (3-X) show very poor durability. This suggests that there is a critical threshold, as opposed to a gradual decline, where beyond a certain level of reinforcement the sorbent is no longer stable.

1.1.3 Chemical and Physical Characterization

Larger quantities of sorbent (~5g) were cycled under TGA conditions in a tube furnace system to produce sufficient material for full material characterization at distinct cycle stages. Characterization methods employed include x-ray diffraction (XRD), BET, and scanning electron microscope (SEM) analyses of the fresh sorbent before cycling, the sorbent after activation, and the sorbent after 25 cycles under the same conditions as in the previous TGA experiments. The latter two samples were collected when the material was in the fully decarbonated state.

XRD

The results of the XRD analysis are shown below in Figure 10. Sample A is fresh, uncycled material. Bound water as Portlandite and carbon dioxide as Calcite are found. Both of these phases are removed during drying/calcining and are not seen in any significant quantities in the cycled materials.

Figure 10: XRD identified phases for fresh material Sample A (top left), dried, calcined, and activated Sample B (bottom left), and 25-cycled Sample C (bottom right) (redacted)

One question is why when fresh material (Sample A) is cycled it initially shows poor absorption that slowly increases until it asymptotically reaches a steady state value, yet when an activated material (Sample B) is cycled under identical conditions it immediately achieves the steady state absorption levels. The XRD analysis suggests that the activation between Samples A and B, beyond removing bound water and carbon dioxide, is actually restructuring remaining stabilizer into calcium oxide and calcium aluminum oxide. To investigate why this change might increase sorbent capacity, we look to the average crystallite size per phase shown in Table 4.

Table 4: Crystallite sizes of identified phases in Samples A, B, and C (redacted)

BET Analysis

BET analyses were performed on the fresh and cycled materials. The fresh material showed a surface area of 7.2 m^2/g, while the activated and cycled materials both exhibited 3.6 m^2/g. This result is observed in the literature, where fresh material exhibits a high surface area which drops significantly upon calcining at 900°C and cycling, however surface area generally continues to drop throughout cycling. The surface area

of PCI's baseline material appears to remain constant from activation throughout cycling, indicating the effect on pore durability of the stabilizing sorbent components.

1.1.4 Three Sorbent Downselect, 100-Cycle testing

Milestones 1.1.1 and 1.1.2

The goal of the high throughput screening was to gain quantitative insight on the influence of stabilizing sorbent components on sorbent performance. From these data, and the trendlines in Figure 14 that show the transient performance of the materials, three sorbents were selected for 100 cycle testing.

The three selected sorbents were TGA tested under accelerated conditions. The samples were first dried at 125°C for 30 min and calcined at 900°C for 10 min under 100ml/min of N_2, then activated at 750°C under 25% CO_2 for 12hrs, and then cycled 100 times between decarbonation at 750°C for 30min under pure N_2 and carbonated at 750°C under 22.5% CO_2 for 60-90 minutes. These tests were replicated three times to meet milestone statistical assessment criteria.

Sorbents 2-1, 1-1 and 1-4 achieved 100 cycle powder testing capacity and durability milestones. Sorbent 2-1 was ultimately selected for pelletizing and extended cycle TGA testing due to high capacity and excellent durability. Additional 100+ cycle testing for sorbent 3-0 was conducted because the capacity of this high CaO sorbent was attractive; however, the sorbent was insufficiently stable for commercialization. This testing was useful, though, as it indicates an upper bound for amount of CaO that can be used in producing a stable sorbent.

The following presents test results for the three selected sorbents.

Sorbent 2-1

Sorbent 2-1 was chosen for near perfect durability and high capacity. The maximum theoretical capacity is 0.50-0.63 g/g.

Sorbent 2-1 exhibits very high durability and sufficient capacity to meet milestone targets. There were no signs of capacity change throughout the entire test. The sorbent did require some additional time to carbonate to achieve the milestone metric, but is still well within the 6-10hrs of carbonation that will be experienced in the commercial system.

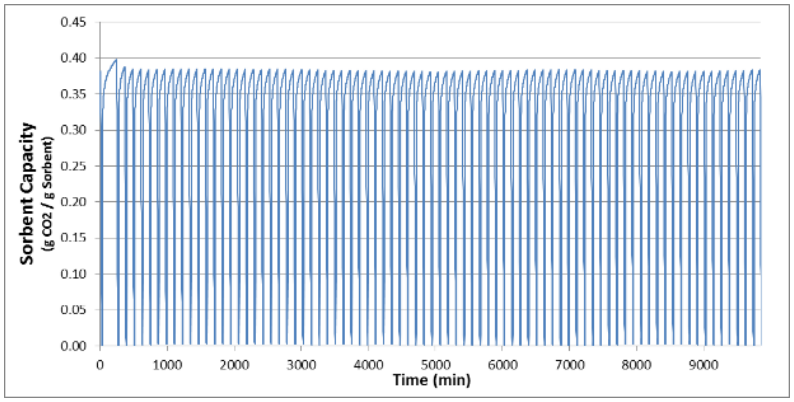


Figure 11: Capacity vs. time for Material 2-1 (example Test A).

Table 5: Capacity and Durability metrics for Sorbent 2-1

Test A	0.3818		count	3	
Test B	0.3803		mean	0.3810	
Test C	0.3810		std dev	7.51E-04	
			std err	4.33E-04	
			CI (alpha)	0.05	
			p value	6.47E-07	Pass
Test A	0.9986		count	3	
Test B	0.9990		mean	0.9981	
Test C	0.9968		std dev	1.17E-03	
			std err	6.77E-04	
			CI (alpha)	0.05	
			p value	2.30E-07	Pass

1.1.5 Sorbent Pelletization

Preparing pellets from powder materials consists of adding a binder material to the powders, and then pressing them (piston-type compressor, extruder, etc.) to form a stable pellet that will maintain its structural integrity. A measure of the mechanical strength of a pellet is its crush strength, and a minimum crush strength is determined based on the specific application. Pellets in packed beds which support the weight of many other pellets, or pellets in fluidized beds, require relatively high crush strengths to prevent pellet collapse and attrition. In the current work, the pellets will be placed in relatively short channels and with low speed gas flows. As a result, very low minimum crush strength is required.

With sorbent 2-1 chosen as the best material composition, a method of pelletizing this sorbent for use in a packed bed reactor was next developed. This involved exploring a set of conditions including moisture content, binder content, compression pressure, and pellet size to best produce a stable and high capacity sorbent pellet.

We began using fully dried and calcined sorbent material and then varying pellet moisture content without any addition of binder, using 31mm dies in a hydraulic hand press pelletizer at a variety of pressures, to produce pellets. We then examined the pellet structural integrity visually after pelletization, and after 24hrs. The majority of these pellets exhibited cracks and were not structurally sound, breaking apart in to fragments and powder in the ambient atmosphere.

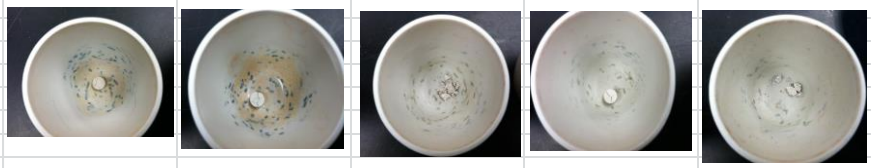
As much smaller pellets are desired at commercial scale in order to maximize packing density, and in order to minimize pellet stresses, a smaller die was then selected for use (6mm). Additional pellets were made, again varying water content and compression force, but also by varying binder content. Pellets that were made under low compression force (~1 MT) and high compression force (~3 MT) exhibited poor structural strength, independent of water or binder content. Pellets made with moderate compression force (~2 MT), with high water content, and low binder content exhibited the best visual structural integrity.

The pellet from Table 6 Column 4 above was broken into small fragments approximately 1mm in diameter, and ~20mg of fragments were put in a crucible and tested in the TGA

under cycling conditions similar to the powder tests to examine uptake capacity and durability.

Table 6: Pellet metrics with 31mm die

Column1	Column2	Column3	Column4	Column5	Column6	Column7
Sorbent Type	1-0	1-0	1-0	1-0	1-0	in house batch
Sorbent Size (um)	<37	<37	<37	<37	<37	
Sorbent (g)	1.0014	1.0014	2.0165	2.0165	2.0165	1.0415
Water (g)	0.05	0.05	0.1	0.1	0.1	0
Binder (g)	0	0	0.2183	0.2183	0.2183	0.1261
Die used (mm)	6	6	6	6	6	6
Force applied (metric tons)	2	1	2	1	3	2
Time in press (mins)	20	18	15	17	15	15
Pellet Density (g/mL)	1.94	1.7	1.97	1.79	1.93	1.88
Appearance	small cracks	lots of cracks	no cracks	cracks	lots of cracks	no cracks
	*fast ramp	*fast ramp	*fast ramp	*fast ramp	*fast ramp	
			ran in TGA on 4/22		ran in TGA on 4/22	



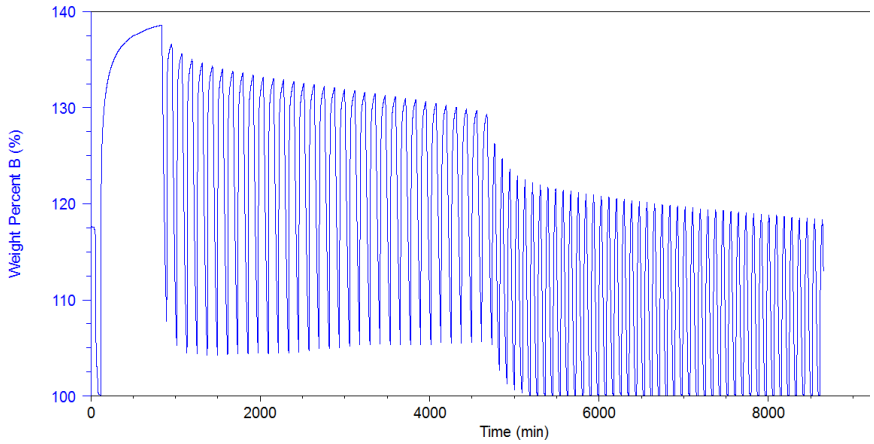


Figure 12: Initial TGA pellet fragment testing

The initial ~4700min of the experiment were conducted by carbonating for 60 minutes at 10% CO_2/N_2 at 700°C, and decarbonating under pure N_2 at 700°C for 60 minutes. It is observed that the material does not fully decarbonate during this period. The mass transfer of the CO_2 leaving the pellet is significantly slower than in powder form, requiring more time for full decarbonation. At ~4700min, the experiment was shifted to only include 30 min carbonation. However, both periods in the experiment exhibit degradation in sorbent uptake capacity. It is believed that along with the slower mass diffusion out of the pellet, there is also slower heat diffusion and the pellet temperature becomes significantly higher than the gas temperature during the exothermic carbonation leading to sintering.

As at this time, the commercial system was expected to use helium as the inert backing gas, as opposed to nitrogen, it was decided to operate the TGA with a helium purge.

The far higher thermal conductivity of helium compared to nitrogen (~4x) was expected to decrease the thermal resistance between the pellet and the gas, and also within the pellet as the helium permeates the particle structure.

In the dual cup TGA, the original powder sorbent and the pellet fragment were tested at the same time for comparison. With helium as the backing gas, the powder is again very stable, even slightly increasing in capacity. Interestingly, the pellet shows much higher reactivity and capacity during the first activation cycle, however continues to lose capacity in subsequent cycles throughout the test (Figure 13).

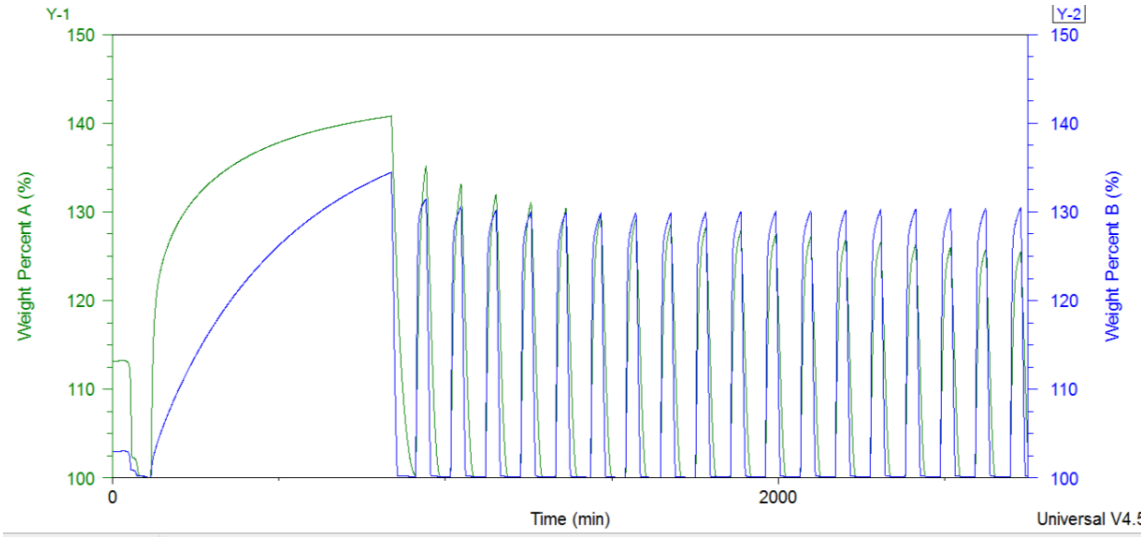


Figure 13: TGA testing of powder (blue) and pellet (green) under helium inert, 7.5% CO_2 carbonation

At 700°C the reaction equilibrium composition is 5.0% CO_2. It was thought that carbonating at 7.5% CO_2 was perhaps too severe resulting in rapid exothermic carbonation. The CO_2 concentration was lowered to 6.0% during the experiment, but as shown in Figure 14, the capacity of the pellet still did not stabilize.

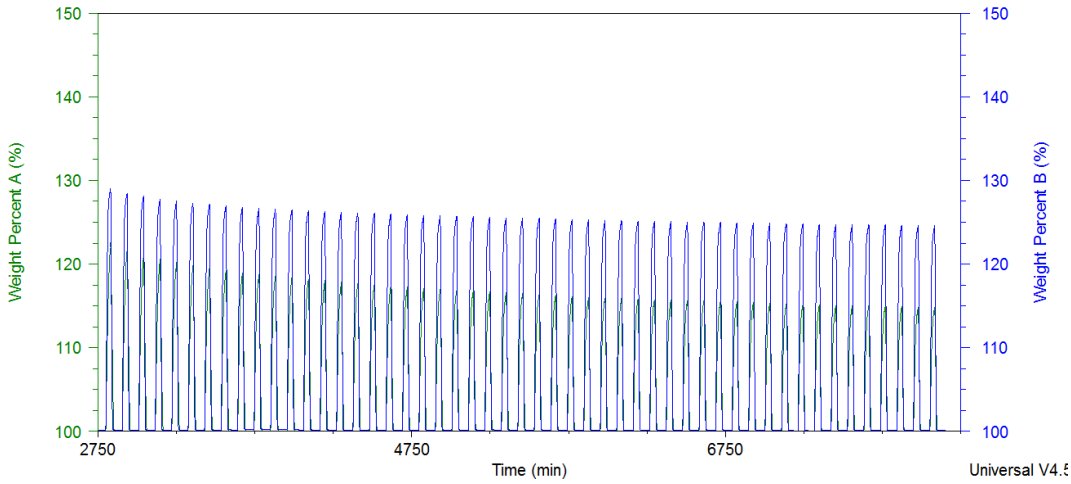


Figure 14: TGA testing of powder (blue) and pellet (green) under helium inert, 6.0% CO_2 carbonation

Further Investigations

With sorbent sample 2-1 chosen as the best material composition, further efforts were made to prepare and test pellets by our partner, PCI, and by Southern Reserach. Pellets were prepared by extrusion using a laboratory syringe with a 0.1" diameter opening. Pellets with no binder, or prepared with colloidal silica AS-30 Ludox binder, were generally not satisfactory. Heat treatments ranging from 100 to 1000 °C yielded pellets with a plethora of shrinking cracks and were prone to powdering. Subsequently, a sample of a calcium aluminate binder (Secar71) supplied by Southern Research was used that yielded superior results. After some method development, a satisfactory procedure for pellet preparation was obtained, although not fully optimized in terms of water or binder contents.

Pellets were tested for CO_2 capacity by two methods. One method was as follows:

- 1 gram placed into a ceramic crucible, place in a box furnace and exposed to 75 SCCM CO_2 or 30 SCCM N_2;
- CO_2 adsorption conducted at 700 °C for 2 hours;
- N_2 treated, to effect desorption, at 900 °C for 2 hours;
- Weight change of pellets measured after each half-cycle.

Results of pellet CO_2 adsorption/desorption cycle testing are illustrated in Figure 15 and Figure 16 for Sample 2-1. Both samples have some variation in both desorbed and adsorbed weights, probably due to insufficient time allowed for complete CO_2 diffusion into or out of pores within the interior of the pellets. This can be overcome through the use of smaller diameter pellets or longer half-cycle times.

Sample 2-1 has nearly constant adsorption weight; the small decrease can be attributed to slight powder formation from sample handling. By way of comparison, Figure 3 presents similar data for sample 2-1 as a powder, without binder. The pellets have lower CO_2 capacity, a bit more so than the dilution of binder can account for, suggesting that the binder may be blocking some of the active CO_2 sorbent.

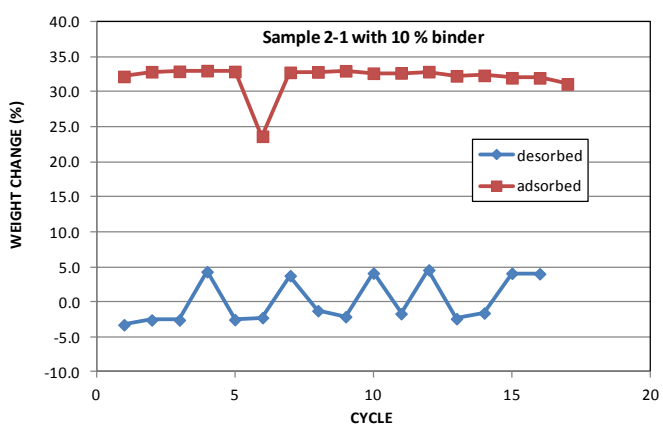


Figure 15 Weight gains measured for sample 2-1 for CO_2 adsorption at 700 °C, 2hours, and desorption, in N_2, at 900 °C, 2 hours.

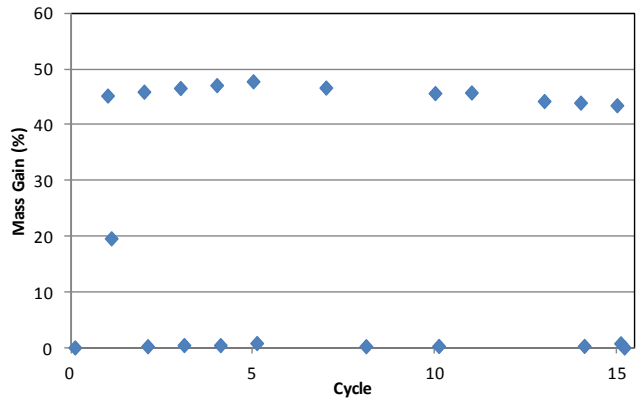


Figure 16. Results for CO2 adsorption / desorption cycles with 2-1 composition powder, no binder.

Sample 2-1 pellet, prepared by the method described here, and the corresponding powder were also run on the TGA. The samples were first heated in N2 to 900°C for 10 minutes, then cooled to 720°C and exposed to 13 % CO2 in N2 fora 12 hours; then the sample was exposed to N2 for regeneration. Then 18, 2 hour cycles were run at 720°C consisting of 1.5 hour carbonation and 0.5 hour regeneration. The results of this testing are presented in Figure 17, and agree with the results presented in Figure 13 and Figure 14. Furthermore, it appears that the pellet capacity is stabilizing with cycling at about 32 g per 100 g.

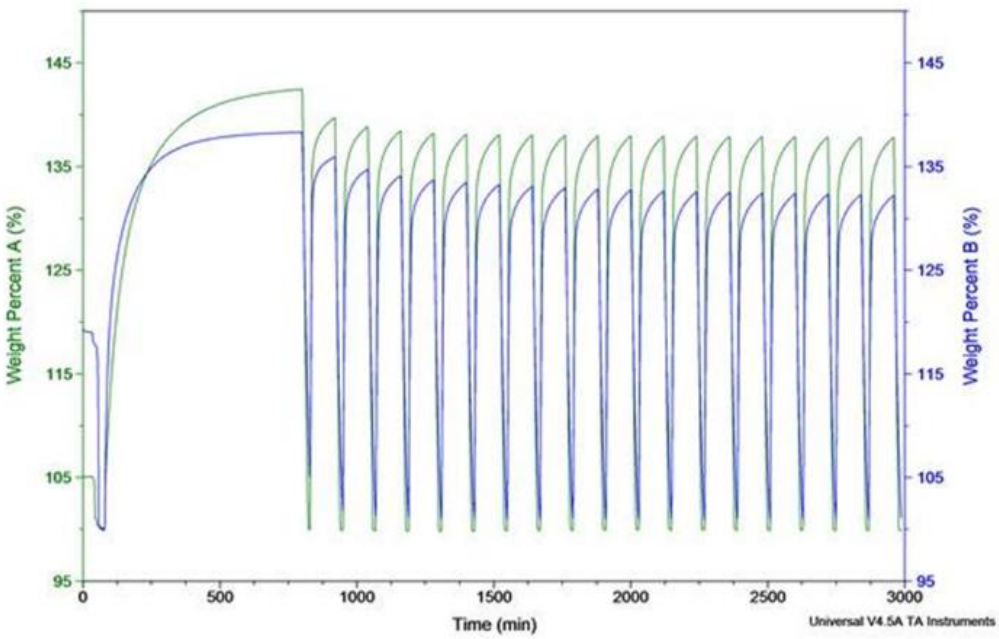


Figure 17: TGA Testing of Sample 2-1 pellet and powder at 720°C.

Pellet integrity was assessed via crush testing before and after adsorption - desorption cycling. Based on this limited testing, the crush strength of the pellets before cycling ranged from approximately 1 to 3 kg. The crush strength after CO_2 cycling ranged from 0.6 to over 3 kg, and on average was the same as the dried material, which is satisfactory strength in the 1 inch channel anticipated

Since spherical pellets of about 1 mm (1/25 inch) diameter are anticipated to be used per study by Manovic and Anthony [2009], it is believed that this will result in an even better performance with the pellets. Furthermore, with 1 mm pellets, it might be possible to reduce the binder content to 5 % which will further improve performance.

1.1.6 1,000 Cycle Pelletized Sorbent Testing

According to the SOPO, Subtasks 1.1.6 (Milestones 1.1.4, 1.1.5, and 1.1.6) was intended to "Test pellets by TGA/DSC and micro-tubular reactor (after crushing to granules) for CO_2 sorption/desorption capacity and kinetics over at least 1000 cycles depending on performance." During simultaneous testing of powder and pellet samples of the same sorbent in the TGA, it was observed that the pellet performance did not match the performance of the sorbent in the TGA. A review of the test procedure led to the hypothesis that pellet testing in the TGA, due to small size of sample and flow of carrier gas in the TGA sample pan, the viability of a TGA test of single pellet samples was questionable. Powder testing was completed up to 350 cycles, but pellet testing in the TGA was aborted, due to significant costs associated with testing and questionable utility of the data. Since the primary application of the sorbent would be in a fixed bed or similar loading form, it was decided to focus efforts on proper testing of the sorbent in a fixed be application in the bench scale unit in Phase 2 of the project. Therefore, this subtask was not completed and milestones 1.1.3 through 1.1.6 were not achieved.

The following is summary of the progress to milestone 1.1.5. The rate of weight gain dw/dt was analyzed for pellet sample 20150517-B in the fresh (average of cycles 9-18) and aged (average of cycles 131-139) states. Figure 18 (left) plots the slope versus total weight gain for fresh and aged samples during carbonation and decarbonation. The ratio of weight gain slope for fresh and aged pellets are given in Figure 18 (right) and Table 7. The carbonation slope is degraded more than the decarbonation slope at all weights, and at small weight gains both carb and decarb slopes are nearly unchanged.

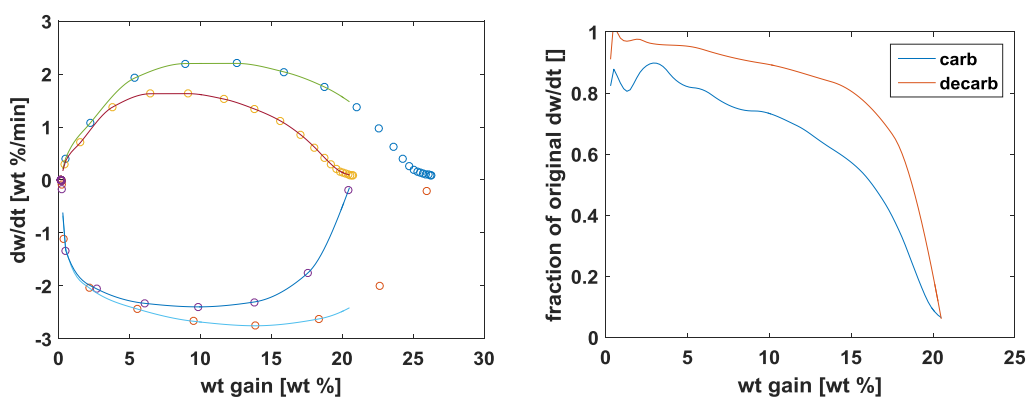


Figure 18: (left) Rate of weight gain versus weight gain for a pellet (20150527-B). Points are measured lines are interpolated. Positive values represent the carbonation, and negative values are for decarbonation. Outer curves are for fresh pellets (average of cycles 9-18) and inner curves are for the aged pellets (average of cycles 131-139). (right) Rate of weight gain ratio of fresh pellets (cycles 9-18) to aged pellets (cycles 131-139) versus pellet weight gain.

Table 7: ratio of wt gain slope for fresh and aged pellets during carbonation and decarbonation

	dwdt_fresh/dwdt_aged	
fraction of wt gain of last cycle (%)	**carb**	**decarb**
0.7	0.86	1.00
25	0.82	0.95
50	0.73	0.89
75	0.56	0.79
90	0.27	0.54

1.2 Reactor Design, Modeling, and Simulation

1.2.1 Chemical Kinetic Modeling

The first step in modeling this system was defining the chemical reaction kinetics of the carbonation/decarbonation process. Numerous reaction kinetics models exist in the literature to express the carbonation of calcium oxide. There are many models that fit data well at a fixed CO_2 partial pressure over a range of temperatures, or at a fixed temperature over a range of CO_2 partial pressures, however none adequately produce a single governing equation to model the kinetics across both dimensions. Through an extensive review of the literature, and analysis of TGA collected empirical data, the project team has developed our own kinetic equation to model the reaction across both dimensions.

$$\frac{dX}{dt} = A_n(C_i - C_{eq})(1 - \frac{X}{X_u})e^{(-\frac{E_n}{RT})}$$

Where: X = Reaction extent (g CO_2 / g Sorbent)
A_n = Frequency factor (n=1 kinetic carbonation, n=2 diffusion carbonation)
C_i = Instantaneous CO_2 partial pressure (atm)
C_{eq} = Equilibrium CO_2 partial pressure at current temperature (atm)
X_u = Ultimate reaction extent (g CO_2 / g Sorbent)
E_n = Activation Energy (n=1 kinetic carbonation, n=2 diffusion carbonation)
R = Universal gas constant
T = Temperature (K)

Constants are able to be calculated for each reaction stage for each of the sorbent materials from empirically collected TGA data. At a constant temperature, it can be seen that reaction rate is a near linear function of CO_2 partial pressure, with rates

increasing as partial pressures move away from equilibrium partial pressures (Figure 19).

As is observed from the empirical TGA data, the kinetically limited surface carbonation and decarbonation reactions are significantly faster than the desired average reaction rate for this system (desired ~6hr process) when operated even marginally away from equilibrium conditions. The much slower mass diffusion limited inner core carbonation is of the appropriate order of magnitude for the average reaction rate. As a result, a reactor channel which operates with a slow moving reaction front has been shown to be better suited than a channel in which all the sorbent reacts at once.

In this design, CO_2 would enter the packed bed at a low flow rate and only surface react with the initial sorbent material. Once this initial region is reacted past the surface limited region, the majority of the incoming CO_2 will pass over the sorbent and react with material further down the channel length. However, as CO_2 flows past this early reacted sorbent, a portion will continue to slowly diffuse through the surface layer and mass diffusion react with the core of the sorbent. As the reaction front moves down the length of the channel, there will be a constant flow of CO_2 over the surface reacted packed bed allowing for both the average and peak heat rates to be achieved.

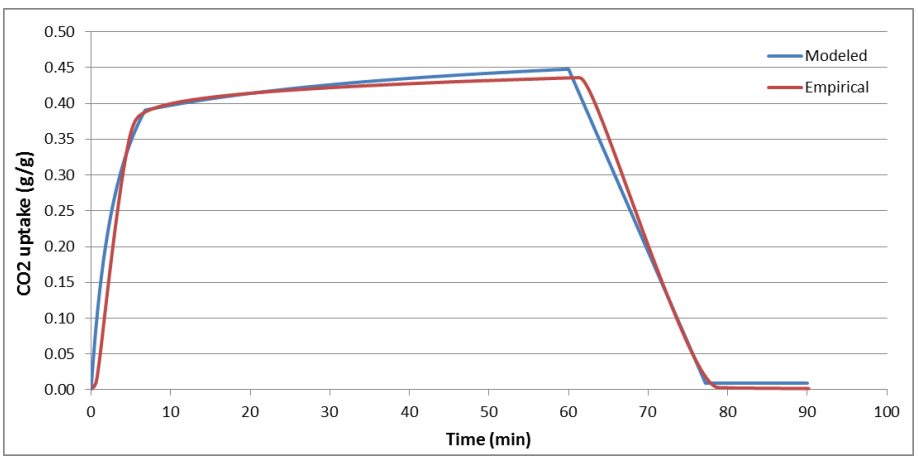
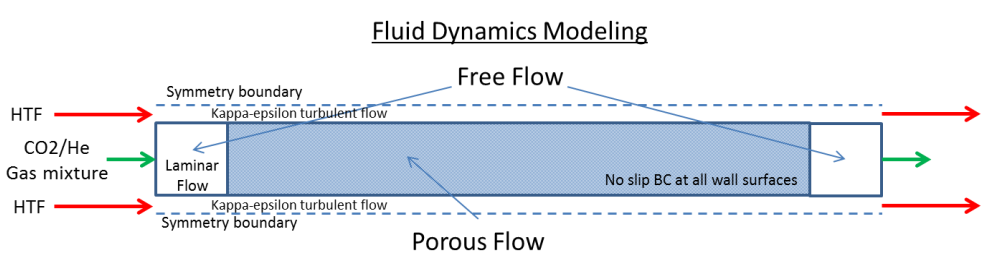


Figure 19: A comparison of empirical and modeled results based on an integrated rate expression to govern reaction rate in all three reaction zones, with dependencies on both temperature and partial pressure and coefficients calculated for each of 3 regions based on empirical data.

Heat Transfer/CFD Modeling

The next step was defining the governing equations and boundary conditions of the CFD and heat transfer environments, as shown in Figure 20.



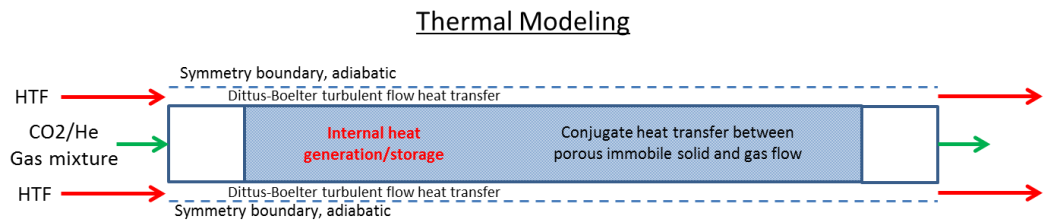


Figure 20: Governing equations and boundary conditions for multi-physics model

An example of HT/CFD modeling of the Sorbent Channel for 6" height, 5 atm absolute pressure, 600°C inlet temperature, and 5% CO_2 with 95%He inlet flow resulted in 90 kW/m^3 uniform volumetric heat generation through porous media with 30%void fraction.

1.2.2 Optimize HTF Tube-side Sizing and Geometry

During evaluation of heat exchanger reactor design, it was determined that, because of the volume of sorbent required, as well as the pressure differentials in the system, particularly on the shell side, if sCO2 was fed into the shell, the cost of shell headers and manifolds would be extremely high, and size of individual reactors would be very limited. As a result, a design modification was made to allow for the flow of sCO2 into the tube side, with the sorbent being loaded within the shell surrounding the tubes. This poses a lightly different problem than the optimization of the tubes from a sorbent loading and heat transfer standpoint, and requires a focus on the optimization of the reactor design, assuming shell and tube, to allow for proper heat transfer within the larger bed. Based on this approach, a revised system design and model was developed, with tube spacing and tube sizing dictated by heat transfer within the packed bed and tube costs.

We have been in direct contact with a specialty alloy tube manufacturer to determine economics for thick walled, high pressure differential capable tubing using alloy 740H, which would be required for an indirect sCO2 to sorbent heat exchanger reactor design. The cost is estimated at 926 [k$/m^3] for 740H tubing at an OD=3/4".This cost basis was used for all calculations of reactor cost with 740H. A Model was created in MATLAB to evaluate the optimal tube spacing, rate of heat transfer and other HX dimensions as a function of tube OD. The model incorporates the effects of pressure and hoop stress as well as degradation and corrosion on piping specifications for the anticipated 30 year life under the proposed operating conditions. As would be anticipated, tube cost decreases with decreasing OD, within specification of standard tubing sizes. However, additional tubes are required to meet overall heat transfer goals. If we assume that OD=¼" is the minimum practical size from a fabrication standpoint, then the minimum tube cost equals 14.3 MM$ for a rating of 750°C. Evaluation of reactor exergetic efficiency indicates that operating at this temperature with this design still allows for reactor-sorbent exergetic efficiencies above 98%. The total cost of the heat exchanger reactor is assumed to be two times the cost of materials, based on manufacturer input, therefore the total cost is 28.6 MM$ at 750°C. Note that significant reduction in 740H cost by 6x will reduce the reactor cost to less than $5,kWh$_{th}$, which may be a

reasonable assumption based on an increased demand due to new high temperature applications evolving over the next ten years.

Budget Period 2

Table 8. Budget Period 2 Milestone Summary

	Metric Definition (From Measurement)	***Success Value***	***Measured Value***	***Assessment Tool***	***Goal Met (Y/N)***	***Notes***
Milestone 2.1.0	Identification of at least one commercial heat exchanger reactor design that can be scaled up to full plant configuration, and can meet the cost target	1	Commercial HxRx design specifications	Third party (commercial manufacturer) verification that heat exchanger design is consistent with sCO2 at high pressures (> 300 bar) and temperature (> 720 °C)	Y	Positive indications received from multiple vendors that temperature, pressure and lifetime requirements are feasible, costs, however, were not able to achieve targets.
Milestone 2.1.1	Maximum difference between peak sorbent temperature and HTF temperature along flow axis in heat exchanger reactor, based on design identified in Milestone 2.1.0 $Tmax, tube - Tmin, sorbent$ (Chargi $Tmax, sorbent - Tmin, tube$ (Dischar	25C	<16ºC from experimental reactor; Modeling Complete: $T_{max} = T_{eq}(P_{CO_2})$	Probabilistic Analysis; wrt sorbent capacity, cycle time, and packing density	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.
Milestone 2.1.2	Specific capital cost of heat exchanger reactor, based on design identified in Milestone 2.1.0 $\$\ Capital\ Cost/kWhr_{thermal}$	10.0	Initial single HxRx: $21.00 +/- 25% Current split system: $5.88 +/-$0.87	Probabilistic Analysis; wrt sorbent capacity, cycle time, and packing density	Y	Quotes from with HxRx manufacturers did not meet cost targets primarily due to cost of materials. A 6x reduction in 740H would see HxRx costs drop to $3.50/kwh. New design & cost estimates of system utilizing ceramic HX and 304H HxRx are complete and partially validated by vendors. Monte Carlo simulation tool constructed, however, magnitude of uncertainty is unknown.
Milestone 2.1.3	Ratio of mass absorbed in final cycle to mass absorbed in initial cycle $Durability = \frac{average\ reactivity\ last\ 50\ cycles}{average\ reactivity\ cycles\ 25-95}$	0.9500; Material shall not be removed from vessel or	0.972 ± 0.015 (>1500 hours of Total Testing at >700C to date)	One-tailed t-test; 95% C.I.	N	Result reported based on 67 cycle test of initial PCI large batch powder pelletized by Clariant, evaluated in 250cc batch in bench unit.

	Over 1,000 cycle test of sorbent in bench scale system, based on design identified in Milestone 2.1.0	treated between cycles in any way				Cycles 16-52 and 53-67 used in calculation. Error estimate is given by $\sqrt{2}\ C/\bar{X}$, where C is the corresponding 95% Confidence interval reported in milestone 2.1.4, and $\bar{X}$ is the reported average from the same.
Milestone 2.1.4	Total CO2 capacity as represented by an average of the CO2 released over the course of the 1,000 cycle test of sorbent in bench scale system, based on design identified in Milestone 2.1.0 $\frac{mass_{CO2\ released,av}}{mass_{initial\ carbonated\ sorbent,av}}$	0.36; Material shall not be removed from vessel or treated between cycles in any way	0.28±0.003 (67-cycle Non-accelerated)	One-sided Student's t-test; 95% C.I.	N	Result reported based on 67 cycle test of initial PCI large batch powder pelletized by Clariant, evaluated in 250cc batch in bench unit. Cycles 16-52 and 53-67 used in calculation. Error estimate is given by $\sqrt{2}\ C/\bar{X}$, where C is the corresponding 95% Confidence interval reported in milestone 2.1.4, and $\bar{X}$ is the reported average from the same.
Milestone 2.1.5	Volumetric energy density = (Total heat released) / (sorbent volume) Total heat released will be measured by the integrated enthalpy rise of the HTF multiplied by its mass flow rate over a single carbonation or decarbonation period	3,000 MJ/m^3	1751±25 MJ/m^3 (25-cycle Non-accelerated, Calculated by CO2 mass balance)	One-tailed t-test; 95% C.I	N	The theoretical ideal limit assuming conversion of all CaO to CaCO3 based on our composition is 2789 MJ/m^3. We have therefore reached 62.8% of that value in the first pellet batch. We anticipate achieving 20-30 % higher value in subsequent pellets prepared by Clariant.
Milestone 2.2.1	Total projected cost (capital + lifetime of sorbent) of TCES system at commercial scale $total cost/kw.hr	15.0	$47.82 +/-$1.75 (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.

1.3 HxRx Reactor Design

Literature associated with heat exchangers for sCO2 power cycles was reviewed. In particular several reviews of heat exchangers for sCO2 applications and heat exchange reactors have appeared in the literature, for example, Musgrove et al. 2012, 2014; Sabharwall et al. 2011; Qui et al, 2011 and others.

Based on these reviews, a matrix of potential heat exchanger reactor configurations and sorbent loading methods was developed that have the potential to meet thermal resistance, sorbent durability, and capital cost targets. The pressure/temperature of S-CO2 power cycle requires considering finned-tube, novel plate/frame, milli/micro channel, and/or printed circuit heat exchanger reactors, in addition to traditional shell and tube type. Additionally, the heat exchange reactor would have to perform under high volumetric reaction rates/heat loading. A list of preferred commercial heat exchanger/heat exchange reactor manufacturers was prepared for discussions of potential heat exchanger reactor designs compatible with sCO2 power cycles (with sCO2 as HTF for the energy storage heat exchange reactor) and the associated requirement of sorbent forming and loading methods into these reactors.

Commercial vendors of viable heat exchange reactors were contacted to determine their ability to meet the commercial pressure and temperature requirements for sCO2 cycle application as well as the requirements for both the ELEMENTS and APOLLO project reactor designs.

1.3.1 HxRx Requirements and Specification

The first step in the reactor evaluation process was to evaluate all the design type variants for HxRx potential. The primary focus here was to determine which reactor types have been identified in literature or product marketing materials as having the ability to meet the sCO2 cycle pressure and temperature requirements. This is summarized in the Table 9 below, with those that have potential highlighted in green. Those with some indicated potential, but little publicly available information are highlighted in yellow and were also candidates to obtain additional information from manufacturers.

Table 9: Reactor Types Having Potential to Meet sCO2 Cycle P and T Requirements

Hx-Rx Type	Max Temperature (deg C)	Max. Pressure (bar)	Applicability Notes
ELEMENTS Single Channel Reactor Spec	*750*	*25*	
APOLLO PILOT Reactor Spec	*750*	*50*	
Commercial TCES Reactor Spec (sCO2)	*750*	*300*	
Shell and Tube	900	300	Feasible, but not compact, resulting in large material costs and capital costs
Plate and Fin (Brazed)	650	30	
Plate and Fin (Diffusion Bonded)	500	200-300	Advances in diffusion bonded systems indicate potential for higher temp applications
Plate (Packinox)	700	300	Improved materials may allow higher T application.
Plate (other - bonded, brazed, welded, gasketed)	900	60	
PCHE	900	400	Feasible, but cost and sorbent loading are potential issues.
Spiral	400	25	

Hybrid PCHE	900	400	Feasible, but developmental.
Microchannel	900	400	Variable specs highly dependent on manufacturer specs

Based on the initial review, the primary reactor designs of interest are: Shell and tube, Plate-Fin, microchannel with larger channel sizes, printed circuit heat exchanger (PCHE), and various hybrid HxRx that include larger channels for sorbent loading and PCHE for heat transfer fluid (HTF). Manufacturers of each type of heat exchange reactor were contacted to obtain specifications and capabilities of each manufacturer's reactor design.

This evaluation and manufacturer discussions, summarized in Table 10, resulted in our effort to validate four primary vendors and approaches. All other vendors contacted could not meet the pressure and temperature requirements.

Table 10: Vendors and Approaches Selected for Further Evaluation

Company	HXRX Design	Pressure Capability (bar)	Temperature Capability (ºC)	Notes	Ballpark bench (250g) HXRX cost
Comprex	PCHE	>200	800	1 mm channels; proprietary packing method	75-100
Heatric	Hybrid (plate-fin + PCHE)	600	900	Utilizes larger channels on one side for sorbent loading. dP requirements may limit allowable channel size, resulting in near PCHE	30-50
Creare	Hybrid (plate-fin + PCHE)	300	800	HX designed for turbine exhaust gas heat recovery (high P and T). Design applicable, with larger channels for sorbent packing, but not originally designed as reactor.	25-50
Various	Shell and Tube	300	900	Shell and tube possible. Alfa Laval-OLMI contacted as primary vendor. Size may be large for required commercial sorbent loading; not well proven at high T and differential pressures.	15-35

Note that all of the designs can theoretically meet the commercial scale reactor requirements. The challenge is to select a viable, optimal commercial system design that also meets cost targets. The high pressure capability of the sCO2 cycle based commercial reactor (not required at bench and pilot scales) is a primary driver for selecting the above reactor types.

Finally, the design of the compact reactors typically results in a cross-flow (rather than concurrent flow) in the heat exchanger. Because of the proposed limitations on the temperature differential of 25C to maintain exergetic efficiency and prevent sorbent damage via hot spots, detailed design and modeling will be required to determine appropriate flow paths within the PCHE type reactor or other reactor options and the ability to maintain the 25C differential.

Further discussion of the potential HXRX solutions for each manufacturer is provided in the following sections.

Comprex

The Comprex heat exchanger reactor is diffusion bonded PCHE whose design was initiated at Chart, but licensed to and further developed by Comprex. The Comprex design has been shown to meet the pressure and temperature requirements for the commercial system. Comprex claims to have developed a proprietary method of sorbent (or catalyst) loading that provides even distribution and packing in the very small (1 mm) channels of the HXRX. This would require that development of sorbent manufacturing methods to meet size requirements for their loading method. Comprex will custom design the reactor to meet our operating conditions and cycle. Comprex recommended stainless steel 304 for the lab reactor and superalloys (Inconel/Haynes) for the commercial reactor.

Heatric

Heatric has multiple designs for high T, high P heat exchanger reactors. Of the three primary designs, the H2X design is most likely to meet requirements for the TCES system. The H2X is a hybrid reactor that utilizes a PCHE layer on the heat transfer fluid side, which can tolerate very high pressures (up to 600 bar), and a plate-fin type of layer on the sorbent side, which can be packed with 1 mm sorbent pellets or spheres and channel size customized to meet operating requirements and specifications. The H2X may have <1mm channels on the HTF side and <1cm channels on the sorbent side, depending on final design requirements. Heatric has built commercial heat exchangers that operate with Helium HTF at 850C and 120 bar.

One issue is the differential pressure between the layers. As the pressures increase and dP increases, the construction of the plate-fin layer requires smaller channels and then ultimately approaches a PCHE (1mm) scale channel, which makes sorbent loading difficult. This system would require smaller particles of sorbent for loading. Heatric recommended Inconel for the material for the bench, pilot, and commercial reactors.

Creare

Creare has designed custom heat exchangers for a variety of customers and provides full engineering, modeling, and design services. Creare is not a manufacturer, but licenses designs to partners and also connects with manufacturing partners to ensure designs can be scaled up to commercial production. Creare has designed a high temperature, high pressure heat exchanger for waste heat recovery from turbines. The proposed design for the U.S. Navy, potentially for shipboard applications, utilizes a hybrid of a PCHE for high pressure HTF and a plate-fin for lower pressure exhaust gas. Although not originally designed for a reactor, the design appears to be directly applicable, similar to the Heatric H2X, with the plate fin side allowing for ease of sorbent loading. The Creare HX has been produced and operated at both a small scale (8”x14” plates) as well as a larger pilot/demo scale unit.

Shell and Tube

Shell and tube reactors can potentially be designed for the required operating conditions. Alfa Laval OLMI has indicated that they would be able to fabricate commercial reactors to meet these requirements. Materials of concstruction

recommended for a shell and tube reactor are Inconel 740H superalloys to meet T and P requirements, along with thicker wall requirements for the shell and tubes, potentially increasing the cost.

Milestone 2.1.1

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 CO2 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 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.

1.3.2 Bench Reactor Design, Construction and Commissioning

Based on the selected tube-in-tube design, an instrumented and insulated skid mounted system with ~250 cc catalyst was constructed and commissioned for bench scale testing. The reaction will be carried out at nominally 720°C which corresponds to the temperature of sCO_2 as HTF in a sCO_2 power cycle. A CO_2/N_2 mixture containing about 2 volume % CO_2 at pressures ranging from 1.1 to 5 bar will be passed over the sorbent bed to control the reaction rate and direction by adjusting only the total pressure. There were significant vendor delays and costs for the booster pump needed for circulating the helium. This resulted in SR canceling the order for the booster pump and making the required design changes to use house-compressed/cleaned air as the HTF in a once-through mode.

A detailed process flow diagram/P&ID and reactor schematic is provided in Figure 21. This shows the details of the design/dimensions and the six-point thermocouple placements on both the shell side and the tube side. The thermocouple is attached using a high temperature metallic paste. This same metallic paste is used around fittings to prevent seizing at high temperature and allow reuse after cooling. Stainless steel berl saddles of ~3 mm size were packed on the shell side. On the tube side, for

commissioning, 3mm alumina spheres were packed. It was confirmed that there was no effect of heating on the berl saddles. It was also confirmed that the reactor could be heated, cooled, then disassembled and reassembled. The volume of alumina packed in the reactor corresponding to a tube OD of 1 inch with .083 inch wall thickness and 32 inches of packed height was approximately 285 cc. Nominal 1 mm pellets were loaded for initial testing.

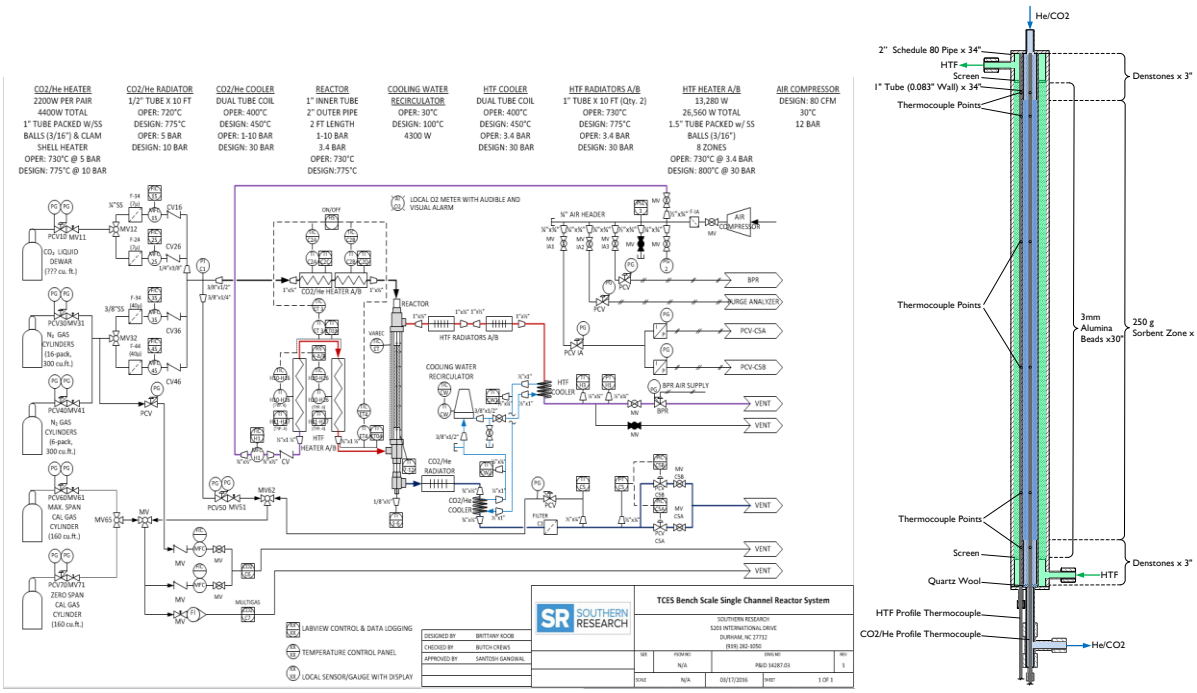


Figure 21: Bench-scale sorbent reactor drawing showing design/dimensions, internals and six-point thermocouples placement on tube and shell sides

Tasks related to the design, construction and commissioning of the bench-scale reactor were as follows.

- System mass and energy balances were completed to determine the range of flows and pressures required to allow both accelerated (2 hours) as well as slow (up to 12 hours) carbonation/de-carbonation cycles. The ranges of potential conditions are listed in Table 11. The conditions are based on achieving 5-10°C change in temperature of the HTF.
- The instrumentation and control system were designed to handle the entire range of flows. Wherever necessary, multiple controls in parallel have been planned to allow the full range to be covered.
- The skid for mounting the system was designed, fabricated and installed.
- A process hazard review was conducted and action items identified and implemented to ensure safe operation and avoids equipment damage or data quality impact.
- The modified CO_2/N_2 and Air HTF heater control panels were installed and tested.

- The HTF heaters and the reactant heaters and radiator coolers were fabricated and mounted in onto the skid.
- Mass flow controllers, back pressure control valves, coolers, instrumentation, etc. were plumbed into the skid.
- CO_2 online analyzers were installed, commissioned and calibrated.
- LabView software was implemented and programmed to control the system, along with a data logger connected to a computer to record data.

All gas lines, valves, sensors, and flow controllers were thoroughly checked with helium for leaks, correct flows, pressures, correct valve direction and operation. Checks were initially performed at 200 psi and then again at 400 psi. The electrical HTF and CO_2 heaters were checked for each heating zone along with the corresponding thermocouples for temperature control. Also each thermocouple and pressure sensor for the monitoring station temperature signals was verified for correctness. Instrument air was verified for correct pressure at each end point and back pressure control valves were operated at varying points for consistent control. The cooling system was also verified for operation and then checked for sufficient cooling with hot gas.

Table 11: Bench Scale TCES System Operating Conditions

Sorbent Side of HEX Reactor	
Temperature	720°C +/-
Total Pressure	1.1 to 5 bar
CO2 Partial Pressure	0.022 to 0.1 bar
Total CO2/He Flow	8 to 48 slpm
HTF Side of HEX Reactor	
Temperature	720oC +/-
Total Pressure	25 bar
Flow	280 to 1680 slpm

The TCES control system is designed for adaptability depending on the requirements of the test plan. A constant set point value or a profile ramp/soak configuration can be the input for the PID control loops of flow rate, pressure, and reactor temperature inlet on both the CO_2 adsorption stream and the heat transfer fluid (air) stream. Also, the operator can select from two differently ranged mass flow controllers and back pressure control valves for the carbon dioxide/nitrogen stream. For data collection, the control system filters the signals as required and then collects the data for further review. The data collected includes reactor temperatures, heater/furnace skin temperatures, reactor feed flow rates, pressures, and the carbon dioxide concentration downstream of the reactor.

Test Results with Alumina Packing

Initial system commissioning indicated that a small amount of heat (supplied by heat tape (~180 W)) was needed to maintain close to isothermal conditions with no internal heat generation. Using the strategy of adjusting air flow on the shell side and also utilizing some external heat using the heat tape, a close approach to the desired operating conditions was achieved as shown in Figure 22. The system has achieved an average of 743.4 °C and 741.4 °C on the sorbent side and HTF side respectively with

maximum variations along the bed of less than 4 °C. Most of this 4 °C variation occurs at the HTF outlet/sorbent side inlet. The scaled schematic below the graph provides a physical reference for the reported data.

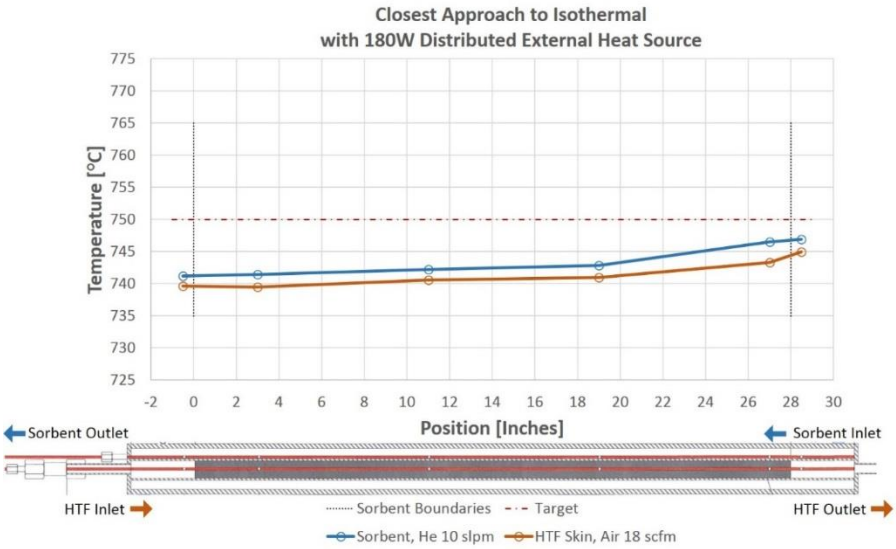


Figure 22: Near isothermal conditions achieved in 32 inch tall reactor with inert alumina packing

<u>Milestone 2.1.2</u>

See section 2.2 technology transfer package for capital costing details.

1.3.3 Sorbent Loading Methods

Sorbent loading method is important to overall reactor design, as it potentially impacts reactor manufacturing requirements. Various loading methods were initially reviewed, including loading on structured packing, similar to catalyst coating, loading pellets, coating reactor walls, and other options. Because the primary driver of the system performance is volume of sorbent, due to the direct relationship between sorbent capacity and energy stored, sorbent loading that achieves a high density is preferred. From an operational standpoint, the simplest methods should also be selected. Therefore, no advantages were observed in loading sorbent in high heat transfer capable packing or structures, and pelletized loading into a packed bed was determined to be the most reasonable approach. The sorbent loading method will affect fluid flow, durability, and heat transfer. Initially the system was designed to have a carrier gas (20-50:1, carrier:CO_2) with a relatively high superficial velocity. This design requires a relatively large pellet diameter (3-5 mm) to minimize pumping power and achieve good control of the reaction. Unfortunately, as we observed from TGA testing of pellets the durability decreases as pellet diameter increases. With the pure CO_2 design the gas velocity is much less and thus smaller diameter pellets with improved durability should be used. Increasing the thermal conductivity of the bed will reduce the amount of heat transfer surface area needed in the reactor. In general this can be accomplished by adding high thermal conductivity filler of various form factors. However, it was not determined that this is required, based on system modeling and bench scale testing.

1.3.4 Bench Scale Tests, milestones 2.1.3, 2.1.4

After more than 1500 hours of bench reactor testing, sorbent capacity averaged 0.283 ± 0.003, with a durability of 0.972 ± 0.015 over 67 commercially relevant 6-10 hour carbonation/decarbonation cycles at >720°C. Figure 23 shows the fractional weight gain at highest capacity for each cycle, showing all 67 cycles completed. Each cycle consisted of commercially relevant 8 hour carbonation and a 7.17 or 7.5 hour decarbonation (cycles 1-8, and cycles 9-72 respectively). Cycles with a shorter decarbonation time show no significant capacity difference from the longer cycles. The linear fit of the fractional weight gain is shown by the solid red line through the data in Figure 23. The shaded regions around the red line indicate the 95% confidence interval in the fit. Dashed red lines above and below the fit show the 95% confidence interval for the mean value based on variability of individual measurements.

It should be noted that the slight upward trend of the data is not statistically significant. This fact is reinforced by the durability metric, which decreased as the test was extended to 67 cycles, and by the 95% confidence interval surrounding the fit, which allows for a neutral or slightly negative slope.

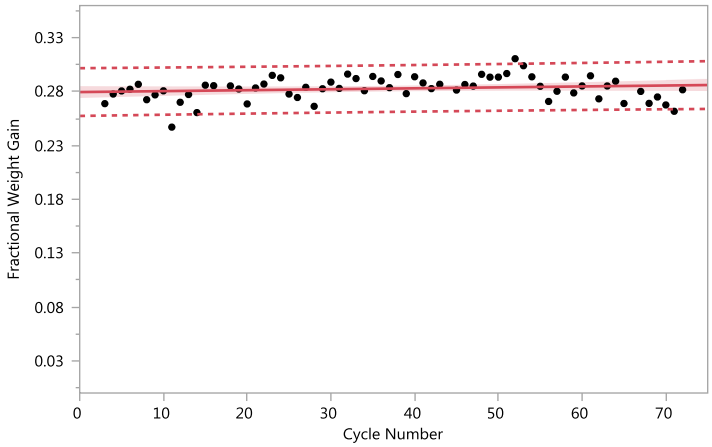


Figure 23: Fractional weight gain by cycle of 0.25L bench scale unit. The linear fit is shown by the solid red line, shaded regions around the red line indicate the 95% confidence interval in the fit. Dashed red lines above and below the fit show the 95% confidence interval for individual measurements.

Based on JMP Life distribution analysis using a Weibull distribution, it may be said with 95% confidence that the worst 95% of cycles will have a capacity greater than 0.236 over a 1,000 cycle lifetime. This statistical analysis informs the probability distribution of likely cases in future Monte Carlo Analysis for the TEA.

Current pellet samples are showing a reduced capacity compared to powders of 30%. This is anticipated, in part due to dilution of pellets with binder (approx. 10%) and reduced surface area of pellets compared to powders. It is unlikely that an improvement in capacity of the sorbent will occur when using the same formula, reagents, production method, and when diluting the product, so the ability to meet this milestone is limited. However, PCI has been able to improve the sorbent powder preparation, and reduce

sorbent variability such that a powder with performance of over 0.4 g/g can be produced. This formulation and method will be transferred for the overall preparation starting from the raw materials. We expect that improved manufacturing methods will improve the capacity of new pellet batches by producing a more homogeneous powder batch and using consistent methodology for pellet manufacture. Optimized binder amount is also under evaluation to see if binder can be reduced to increase the overall capacity of the pellets. In addition, Clariant will evaluate production methods beyond just pellet extrusion to determine if other methods (i.e spray drying) can improve pellet surface area, size distribution, and other characteristics.

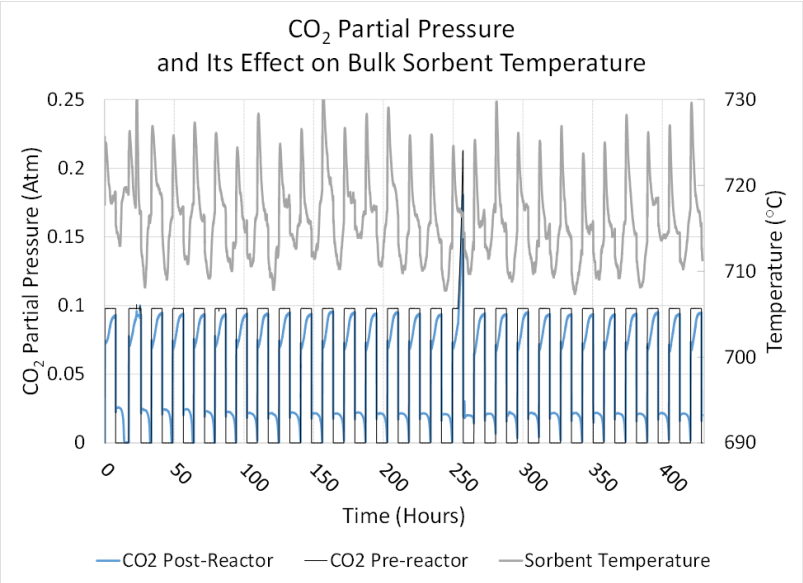


Figure 24: The first 28 cycles of extended testing on the bench scale unit, including some initial process adjustments (1 & 2) and one process excursion (17). The difference in CO_2 partial pressure between pre-reactor (black) and post-reactor (blue) indicates the amount of CO_2 absorbed or released by the sorbent. The corresponding temperature change (gray) shows the response of the sorbent bed. Note the maximum temperature change is well below ±25ºC from the average.

The average temperature within the sorbent bed was 714.6°C, and 707.8°C in the HTF. An average sorbent bed temperature change of +6.1°C / -7.0°C was observed during carbonation and decarbonation respectively. The HTF temperature change in response varied from +3.1°C to -4.3°C during carbonation and decarbonation respectively (Figure 24). Further investigation has suggested a vacuum system rather than a diluent gas would be more practical for the commercial scale plant. As a result, no CO_2 will be introduced during decarbonation. This will allow the diluent gas to more accurately mimic the effect of the vacuum system. The sorbent bed was operated at 55.83 PSIG, with 24.5 slpm of Nitrogen and 500 sccm of CO_2, or 2% CO_2, during carbonation. During decarbonation CO_2 flow was cut off, Nitrogen flow was raised to 25 slpm, and the pressure was raised to 79.4 PSIG. The increase in pressure was done to decrease the decarbonation rate in accordance with the goal of longer cycle times laid out for the milestone. The HTF was maintained at a constant mass flow of 8 scfm at 3.0 PSIG.

Unfortunately, it was not possible to meet the milestone of achieving a 1000 cycle test within the Elements project budget and timeline. Based on the most rapid cycling of the

system to date, the test would take over 6,750 hours, or approximately 9½ months. In order to complete the test in a reasonable time-frame accelerated cycling is necessary.

An internal research and development project has begun to test the as loaded sorbent under accelerated conditions, outside of the bench scale unit. This project is being supported independently by Southern Research. A TPD (temperature programed desorption) will be used to simulate the larger bench scale unit. The TPD has been loaded with 300mg of pelletized sorbent, and cycling has begun with a total flow of 95 sccm, 9.7% CO_2 at 1 atmosphere during carbonation, and 0% CO_2 during decarbonation, with the balance always made up by nitrogen. Complete cycles are 160 minutes long, split evenly between carbonation and decarbonation. Testing will continue for as long as possible, up to 1,000 cycles, to probe sorbent durability over the long term.

Milestone 2.1.5

Based on the average capacity of 0.278 g CO2 /g sorbent for the first pellet batch, and knowing the density, a volumetric energy density of 1751 MJ/m^3 of sorbent has been estimated which is about 63 % of the theoretically achievable energy density for the sorbent composition being tested/scaled up. With the new batches entirely prepared by Clariant we anticipate that we will be able to achieve 20 to 30 % higher energy density than achieved by these first pellets.

1.4 Technology Transfer Package

Southern Research has developed a technology transfer package that summarizes the publicly available information regarding the TCES system. The technology transfer packages consists of the following items

1) public version of this report
2) marketing brochure / fact sheet
3) Most recent public presentation

In addition, Southern Research is developing both a proprietary and non-proprietary 'Pitch Deck' presentation that includes a summary of the TCES system concept, development status, funding levels received and anticipated funding required for next level of development, and system economics / finances. The intent of this presentation is to provide necessary information to potential investors (companies, venture capital, and other investors).

Southern Research has presented information on the TCES system at multiple conferences and in the press, including the following:

April 2014: Sunshot Grand Challenge poster

July 2014: Press Releases (picked up by 14 publications)

July 2014: ASME Energy Sustainability presentation

February 2015: ARPA-E Summit Showcase Presentation

February 2015: ARPA-E Summit Showcase Presentation

June 2015: ASME Power and Energy presentation

June 2015 SolarPACES presentation

July 2015: UNC SERC poster

July 2016: ASME Charlotte presentation

During the development of this technology (to date), Southern Research has developed relationships with several potential technology end users, equipment suppliers, and other partners. As a result, several non-disclosure agreements have been signed with these entities that will allow for further exchange of information with the companies and discussion of the technology, intellectual property, and potential commercialization and development pathways.

1.4.1 Reactor and Balance of Plant Cost

The milestone target in Milestone 2.1.2 and 2.2.1 represents the expected capital cost per installed $kWh_{thermal}$ for the heat exchange reactor and the entire plant respectively. Capital costs shown here contain the cost of purchasing equipment, 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 balance of plant (BOP) (including 36% contingency, fees, debt service, etc.) is $36-42 /kwh assuming up to 50% reduction in future development costs for specific pieces of equipment that are not on the market or commercially available currently. The initial design for the thermal storage system had an integrated heat exchange reactor (HXRX) operating at increased pressure with CO_2 in a carrier gas, with gas storage operated at high temperature and similar pressure ranges. This would require high temperature high pressure gas storage and a high temperature booster compressor to meet system design requirements. Unfortunately, current designs for such systems are developmental and extremely cost prohibitive. Costs incorporating these types of systems were on the order of $80/kWhth or greater.

To reduce gas storage requirements – both physical space and temperature and pressure, designs were evaluated that allowed for utilization of pure CO_2 as the reactant, operating at sub-atmospheric pressures. To again reduce gas storage physical space and material requirements, gas storage operations where designed to occur at 25 bar. This required pulling a vacuum on the reactor, then re-pressurizing the gas to 25 bar for storage. Additional systems designs were evaluated that had the system include a single high temperature, high pressure differential heat exchanger reactor, with other designs evaluated utilizing a separated high pressure differential heat exchanger and a low pressure differential heat exchanger reactor. Figure 25 shows the ASPEN simulation PFD of the single HxRx system.

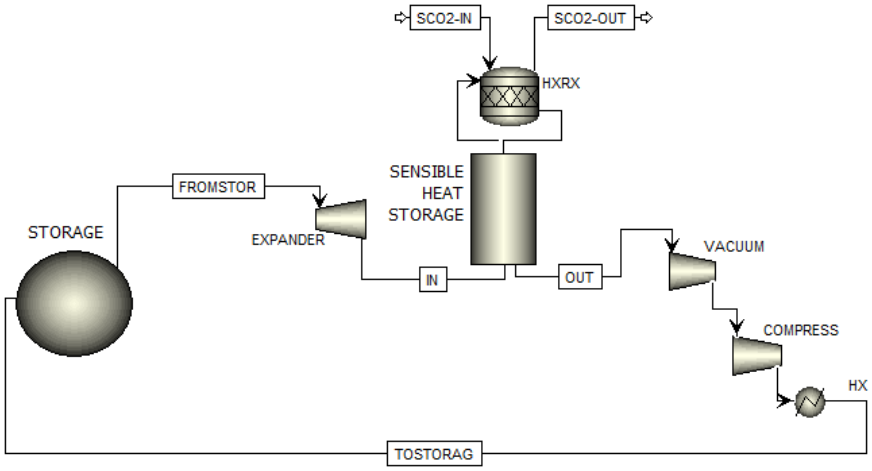


Figure 25: ASPEN PFD of Original System Design

Table 12 compares the integrated HXRX with some of the quotes for the bifurcated system received from vendors. Comprex and Alpha Laval quotes were based on a helium heat transfer fluid, while the Ceramatec 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 Comprex and Alpha Laval heat exchangers could be reduced (alternatively, if the □T across the reactor could be increased, it would also decrease the size and cost of the HXs). The proposed costs for metal alloy based reactors and heat exchangers is based on current costs for Inconel 740H.

Table 12: Installed Reactor System Costs (Current Material Prices)

HX+Low Press. HXRX or High Press. HXRX	**Reactor Cost w/ Comprex HX (He HTF)**	**Reactor Cost w/ Alfa Laval HX (He HTF)**	**Reactor Cost w/ Ceramatec 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
Total Reactor Costs	**$80,386,000**	**$138,786,000**	**$11,767,584**	**$42,000,000**	**$13,400,000**
Reactor Costs per kWh	**$40.19**	**$69.39**	**$5.88**	**$21.00**	**$6.70**

The first pass at the capital cost estimate done with ASPEN for the remaining balance of plant (BOP) showed that the built in equipment cost for the 25 bar CO_2 storage case 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 13 shows the results of the pressure sweep rough analysis. The analysis identified atmospheric gas storage in inexpensive vinyl buildings as a potential alternative near term solution.

Table 13: Results of pressure sweep analysis for solar storage BOP costs.

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	**$79.93**	**$1,484.82**	**$42.47**	**$98.27**	**$46.04**

Figure 26 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 as provided by a quote from Oerlikon-Leybold. Additionally, the vinyl storage was also provided through a quote from Membrane Structure Solutions, for 16 half-dome structures (d=100', L=650', h= 50'). Both of these items, but especially the vacuum pump could see significant 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. Additionally, it is expected that if the cost of 740H is reduced to about 1/6th its current cost then the total plant capital costs can reach the $15/kwh target.

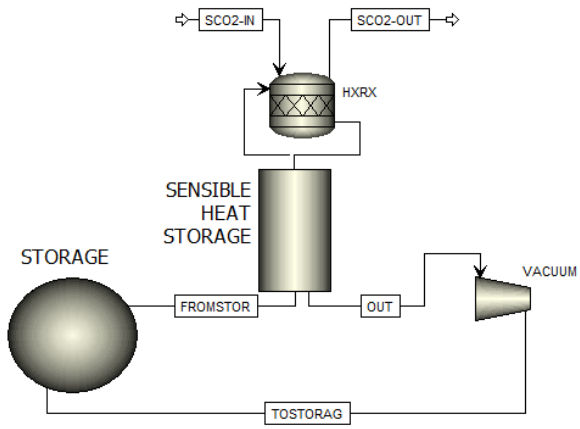


Figure 26: ASPEN PFD of 1 bar storage case

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 14 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 14: Monte-Carlo Simulation of installed equipment costs.

	Vacuum Pump	Storage	RXHX	BOP	Cont & fees	Total Cost
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
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. With additional reductions in materials of construction costs, the $15/kwh is attainable.

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 project:

- 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 that provided the best combination of capacity and durability.
    -
- Production of the sorbent in a significant quantity and in a form (pellets) that is viable for loading into the proposed heat exchanger reactor designs.
    - The pelletizing sorbent generally decreases the durability of the sorbent, smaller pellets will have increased lifetime at the expense of higher pressure drop.
    - Particle size is critically important but was not explicitly optimized as its own variable. An opportunity exists to control the particle techniques such as spray drying to give a size range of (40-150 um)
    - Pelletizing inherently leads to reduced performance as compared to powder due to incorporation of binder and reduction in surface area.
    - Sorbent performance and cost have a less significant impact on system economics at this point than balance of plant and reactor costs.
- 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 sCO2 cycle applications.
    - Operation of the sorbent reactor at lower pressure can provide design benefits, but results in added costs for both a heat exchanger and the heat exchanger reactor. Separation of the reactor and power block heat exchanger reduces engineering requirements for the reactor (and associated material costs).
- Completion of integrated system design for commercial applications to meet system performance requirements and a path forward to potentially meet cost targets.
    - Significant costs and engineering are required to manage CO_2 storage after decarbonation. System designs have been altered to provide reasonable costs based on currently available technologies, including incorporation of ambient storage solutions with sensible heat recovery to maximize system efficiency.

    - 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.
- Because of the conditions associated with operation at high temperatures and high pressure of a sCO_2 cycle, system costs, specifically associated with high temperature materials, are extremely high. Requirements for use of superalloys such as Inconel 740H result in reactor costs that exceed current targets. In addition, high temperature gas storage and compression options are limited in current commercial applications. With growing markets, costs of these materials and equipment should be reduced significantly and a path to a commercial cost below the $15/kWh target is likely achievable. However, those cost reductions must be achieved.
- Using standard alloys, such as 304H stainless steel would allow the system as designed to operate within temperature ranges below 700C, which would be applicable to current CSP system designs and would be cost competitive with current molten salt storage system prices.

Inventions, Patents, Publications, and Other Results

All publications are listed in Section 1.4. 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.

Path Forward

Ongoing research and development of the calcium oxide based high temperature thermochemical energy storage system continues under the DOE APOLLO program, focused on scale up of the system detailed in this report to a much larger system, on the order of 400+ times the thermal storage capacity of the existing bench scale unit. In addition, further validation of the pelletized sorbent and production of larger batches is underway.

Additional discussions have been held with multiple reactor technology developers, sorbent supplier (PCI), sorbent manufacturer (Clariant), and potential end users (CSP manufacturers, major utilities, oil and gas industry, and investment groups regarding potential paths forward. Currently, multiple entities have expressed interest in evaluation of a system that would potentially work with steam cycles, at lower temperatures than those observed in the sCO_2 cycles. With the interest expressed, significant additional scale up efforts beyond the current bench and planned pilot scale should be pursued.

- Suggestions for further research and development include:
    - Further optimization of the sorbent design, specifically associated with pelletization, including optimization of pellet manufacturing methods, minimization of binder use, and optimization of pellet size range, while ensuring sorbent capacity and durability continue to meet targets;

- Development of a range of sorbents of similar design and reaction function that work across a range of possible storage application temperatures, including a primary focus on sorbents functioning in the 450-700C range.
- Further evaluation and development of potential gas storage options to reduce costs and physical constraints associated with high temperature gas storage. Options to investigate could include separate sorbent beds for thermochemical storage of CO_2 at lower temperatures.
- Development of more cost effective high temperature materials for reactor and component development as well as high temperature heat transfer fluids.
- Scale up of the TCES system to a small pilot unit with continued operation under on-sun conditions. Continued scale up to a large demonstration facility operating on a slip stream of output from a CSP facility for an extended period of time.

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