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# Carbonate Composite Sorbents: A Novel Technology for Biogas Upgrading

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**ABSTRACT:** With no signs of slowing, global warming and resource consumption continue to rise. Biogas has been shown to be a reliable renewable energy source in tandem to natural gas. Biogas is naturally sourced as a byproduct from dairy and food waste plants and can be upgraded to biomethane as an alternative to natural gas. Lawrence Livermore National Laboratory (LLNL) has developed carbonate composite sorbents which yield pipeline quality biomethane and cost less than traditional biogas upgrading technologies (e.g., water/chemical scrubbing, pressure swing adsorption). Laboratory-scale experiments using biogas and the composite sorbents resulted in absorption of 0.62 mol of CO<sub>2</sub> per kilogram of material, methane purity of >99% and an energy demand of <0.1 MJ/Nm<sup>3</sup>. The team is currently working on scaling up the production of the composite sorbent to kilogram quantities and to operate a small-scale pilot at a partnered test facility. To ensure market competitiveness, the team is currently working on improving the CO<sub>2</sub> loading capacity of the composite sorbent by optimizing the powder to polymer ratio and developing a confined coaxial powder extrusion method. This formulation is proprietary to LLNL. IM release number: LLNL-TR-835543.

## INTRODUCTION

As the world continues to emit greenhouse gasses (GHGs) researchers continue to try and find more viable solutions to mitigate the effects of climate change. Due to the rise of GHGs, there have been increases of 47% in carbon dioxide (CO<sub>2</sub>), 56% in methane (CH<sub>4</sub>), and 23% in nitrous oxide (N<sub>2</sub>O) in the atmosphere since 1750, motivating scientists to increase efforts for the research, development, and production of carbon capture and renewable energy technologies.<sup>1</sup> Although carbon capture and storage (CCS) is regarded as one of the most straightforward and practical solutions to reduce global warming, CCS is often not viable due to increased energy requirements and other adverse effects on the surrounding environment.<sup>2</sup> Adverse effects on the environment from CCS include potential leaching or spilling of CO<sub>2</sub> during transportation for sequestration, poor air quality around the plants due to dust suspension, and potential to induce seismic activity, all which can negate the benefits of cleaning the air.<sup>2</sup>

In addition to advances in more well-known renewable energy sources (e.g., wind and solar), an upcoming and exciting potential renewable energy source is biogas. Current applications for biogas include engine-based combined heat and power plants and a replacement for natural gas and vehicle fuel (biomethane).<sup>3,4</sup> Biogas is abundant and is naturally produced through anaerobic digestion of agriculture activities, wastewater treatment plants, and landfills. The composition of biogas is approximately 45-70% CH<sub>4</sub>, 30-55% CO<sub>2</sub> and additional gasses such as hydrogen sulfide (H<sub>2</sub>S), water vapor, ammonia (NH<sub>3</sub>), and nitrogen (N<sub>2</sub>).<sup>5,6</sup> The relative percentages of each gas depends on the raw materials and the physical/chemical environment of the anaerobic digestion. Like natural gas, biogas contains a high percentage of methane which can be further refined or “upgraded” to biomethane. Since CH<sub>4</sub> is combustible and produces energy when burned, removing CO<sub>2</sub> through carbon capture technologies increases the energy content per unit mass/volume

(caloric value) of the biogas.<sup>7</sup> The presence of CO<sub>2</sub> and other contaminants (e.g., H<sub>2</sub>S) in biogas can also limit storage and inhibit transportation due to freezing and corrosivity to metallic parts at low concentrations thus shortening the lifetime of expensive equipment.<sup>7</sup>

Current technologies to upgrade biogas are categorized into several different categories such as absorption, adsorption, membrane separation, and cryogenic separation. Absorption is further divided into two different categories physical and chemical adsorption. Physical absorption includes methods such as water scrubbing which relies on the intermolecular forces between the gaseous molecules of CO<sub>2</sub> and liquid molecules of water and requires high pressures and low temperatures to increase the solubility of CO<sub>2</sub>. Chemical absorption involves the use of organic/inorganic solvents to separate CO<sub>2</sub> and methane and relies on the covalent bonds between the gas and the molecules of the absorbing liquid.<sup>8</sup> Additionally, chemical scrubbing often uses amines because of their physical and chemical reactivity with CO<sub>2</sub>. While amines often offer advantages over water scrubbing, the regeneration process of the amines is energy intensive, corrosive which can ultimately lead to the degradation of the amines.<sup>8</sup> This process would not be economically feasible for small scale CO<sub>2</sub> absorption at dairy and food waste plants or for high concentration streams of CO<sub>2</sub> such as biogas upgrading.

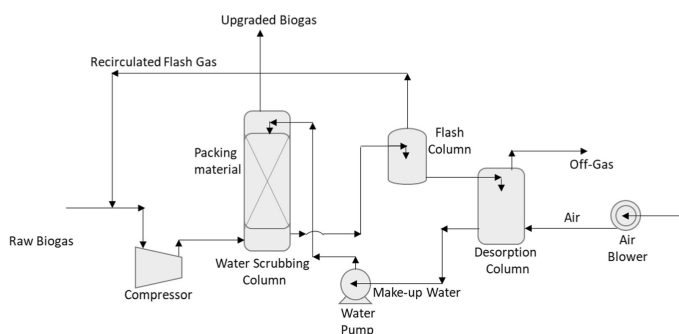
Adsorption relies on the mechanism of gas molecules being selectively adsorbed to solid surfaces according to molecular size.<sup>9</sup> Pressure swing adsorption uses van der Waals forces and differences in pressure to transfer solute in a gas stream to adsorbent material.<sup>10</sup> Like chemical scrubbing, pressure swing adsorption is also energy intensive comparatively and requires extensive process control to achieve higher methane concentrations.<sup>10</sup> An alternative to scrubbing and adsorption is membrane separation which relies on the permeability and selectivity of the membrane material.<sup>10</sup> These membranes are often polymeric and suffer from trade-

offs between selectivity and permeability, as well as, plasticization at higher pressures.<sup>10</sup> Other novel carbon capture techniques include biological methods (e.g., hydrogenotrophic methanogenesis), in situ biogas upgrading, hybrid methods, and other absorbent materials.<sup>7,10</sup> This paper will focus on the development of composite sorbents compared to water scrubbing, the most common method, and membrane separation for biogas upgrading.

## CURRENT STATE OF TECHNOLOGY

### Water Scrubbing

Water scrubbing is the most widely used method in industry to remove CO<sub>2</sub> from biogas and relies on the different solubilities of CO<sub>2</sub> and CH<sub>4</sub> in water.<sup>11</sup> To remove CO<sub>2</sub> from biogas, the biogas enters through the bottom of a pressurized packed column while water flows opposite to the biogas to maximize the gas-liquid contact area (Figure 1). The water is then put back into the environment (single pass) or depressurized and run through a stripping column in atmosphere to remove the CO<sub>2</sub> and be recycled (regenerative absorption).<sup>7</sup> If the concentration of H<sub>2</sub>S is high enough, during desorption, H<sub>2</sub>S can oxidize to H<sub>2</sub>SO<sub>4</sub>, cause corrosion, and decrease the lifetime of the equipment.<sup>11</sup>



**Figure 1.** Flow diagram for water scrubbing of biogas with regeneration of water.<sup>7</sup>

If water scrubbing plants wanted to reuse water, having to replace equipment more often is a costly expense, thus a pretreatment to remove the H<sub>2</sub>S may be required.

Another advantage to water scrubbing is high methane purity (94-98%) which is critical for countries with high purity biomethane regulations such as Sweden (97%), Switzerland (96%), and the United States ( $\geq 96\%$ ).<sup>5,12,13</sup> Additionally, water scrubbing does not require the use of any harmful or expensive chemicals since the process relies on the physical absorption of the gasses into water.

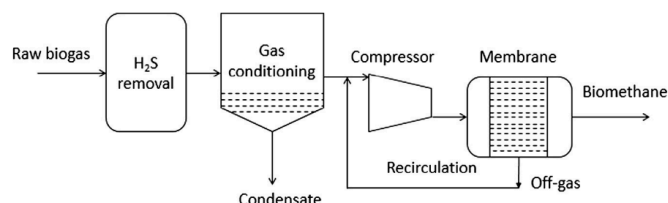
While water scrubbing is less energy intensive and more environmentally benign than the other methods of upgrading biomethane, this method can be bulky (i.e., requiring multiple tanks) and takes longer than other upgrading methods. The upgrading plant may also have to make trade-offs between energy usage and water requirements depending on the resources available. To achieve high purity CH<sub>4</sub> (>90%) with pressures under 10 bar, substantially large quantities of water and larger columns would be required.<sup>7,11</sup> Additionally, if the plant decides to recycle the water, this requires another tank or desorption column which has equal energy

requirements as the absorption column due to the main energy demand is from pumping water.<sup>11</sup> The energy demand also depends on the different pressure levels of each tank and how many times the gas and water have to be pressurized and depressurized. On the other hand, operating machines and pumps at high pressures requires low water flow rates and increases the cost for biogas compression and water pumping which in turn decreases the lifetime of the plant.<sup>7</sup>

### Membrane Separation

Membrane technology relies on a permeable barrier that allows specific compounds to pass through in a controlled manner depending on the concentration, pressure, temperature, potential, or the specific compounds. Mass transport through a membrane is governed by gas diffusion along the membrane and flow of the gas through the porous membrane.<sup>10,14</sup> For biogas upgrading, typically CO<sub>2</sub> will permeate through the membrane while methane remains on the inlet side.<sup>10</sup> The most common membranes for CO<sub>2</sub> biogas upgrading are polymers and other inorganic materials, but in practice, polymers are used the most.<sup>15</sup> These polymers include polyamide, polyimide, cellulose acetate, and polydimethylsiloxanes (PDMS) which have excellent mechanical strength, are easy to manufacture at low costs, and have selective permeation.<sup>10</sup> Figure 2 depicts a flow diagram for a typical membrane separation setup. The raw biogas first goes through an initial filter to remove H<sub>2</sub>S and other contaminants such as water, oil droplets, and aerosols. Then the processed gas moves through the membrane which typically consists of multiple membranes either in series or in parallel depending on the industrial site. The resulting biomethane is then separated while the off gas is either recirculated or vented to the atmosphere.

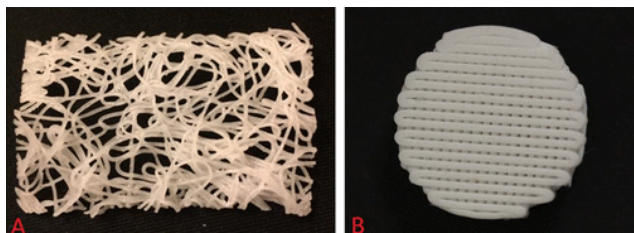
Some advantages to membrane separation include no chemical use, low mechanical deterioration, and low spatial requirements. Membrane separation can achieve anywhere from 85-97% methane purity but can also have methane loss anywhere from 1-13%.<sup>9</sup> On the other hand, some disadvantages include additional gas pre-purification, tendency to have higher methane losses, and the membranes exhibit unstable long-term behavior.<sup>15</sup> Plasticization by CO<sub>2</sub> occurs readily with many glassy polymers as the polymer expands upon CO<sub>2</sub> absorption increasing the free volume and segmental mobility. This increase of free volume allows for increased permeation of methane but, in turn, the polymer loses selectivity.<sup>16</sup> Polymers with polar or flexible pendant groups sometimes lead to higher plasticization or favored CO<sub>2</sub> solubility due to stronger dipole interactions with the polarizable CO<sub>2</sub> molecules.<sup>16</sup> Therefore, polymer membranes with high will eventually lose selectively over time.



**Figure 2.** Flow diagram for membrane separation.<sup>10</sup>

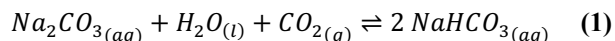
## Current Work – Composite sorbents

Lawrence Livermore National Laboratory (LLNL) has recently developed a new class of sodium carbonate and silicone sorbents which have promising selectivity to capture CO<sub>2</sub> and provide natural gas pipeline quality biomethane. Due to their chemical nature, these composites are nontoxic, cost effective, and require low regeneration energy.<sup>5</sup> Additionally, LLNL showed the material is easily extruded or 3D-printed into different high surface area morphologies to improve CO<sub>2</sub> absorption and selectivity (Figure 3).



**Figure 3.** Sodium carbonate PDMS composites that were (A) hand-extruded from a 410  $\mu\text{m}$  diameter tip and (B) direct ink write printed from a 580  $\mu\text{m}$  diameter tip.<sup>5</sup>

The active ingredient of the composites includes aqueous sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) embedded in polydimethylsiloxane (PDMS)-based polymers. The composites rely on the chemical reaction between the carbonate, water, and CO<sub>2</sub> gas. The absorbed CO<sub>2</sub> is then temporarily store as aqueous sodium bicarbonate within the PDMS-based polymer (Equation 1).



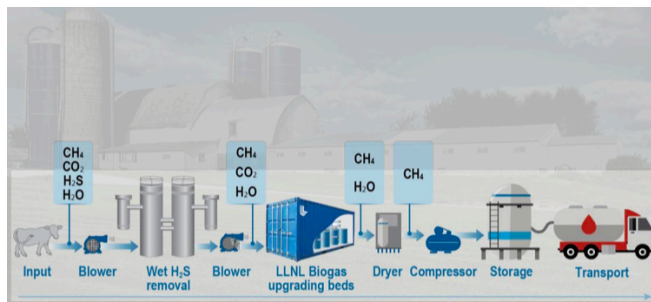
This combination of materials was chosen for their 3D printability and high CO<sub>2</sub> permeability.<sup>5</sup> Murialdo *et al.* found that the composite sorbents absorbed 0.62 mol CO<sub>2</sub> per kilogram of material with methane purity >99%, pipeline-purity natural gas.<sup>5</sup> Additionally, the energy demand of these composite sorbents is <0.1 MJ/Nm<sup>3</sup> of raw gas, which is much less than other traditional upgrading technologies due to ambient pressure, less expensive equipment, less cost downstream for gas compression, and taking advantage of the natural concentration gradient between the biogas stream and ambient air.<sup>5</sup>

Another advantage of these composites includes the ease of sorbent regeneration especially in contrast to water and chemical scrubbing. The composite sorbents are easily regenerated by simply flowing humid room temperature air through the reactor. Murialdo *et al.* reported the time to fully regenerate the sample is approximately inversely correlated with the air flow rate and also scales with the quantity of CO<sub>2</sub> to be desorbed.<sup>5</sup> This process keep expenses low because the absorption and desorption are run in ambient conditions which cuts back on cost for heating system and expensive equipment needed to handle high pressures.

## PROJECT SCOPE – COMPOSITE SORBENTS

With a capital expense around \$700-1,300 per m<sup>3</sup>/h, the composite sorbent upgrading method is approximately one-third the cost of water scrubbing at \$2688-3071 per m<sup>3</sup>/h.<sup>17,18</sup> LLNL demonstrated at the laboratory-scale that these composite sorbents were capable of delivering pipeline quality

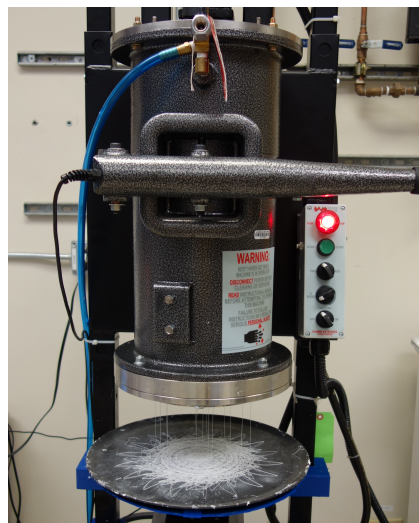
methane using simulated biogas, with the ability to be repeatedly regenerated in ambient conditions during 1000 h. LLNL plans for a commercial demonstration with the intention for the commercial-scale technology to be available in the future for additional sites (Figure 4).



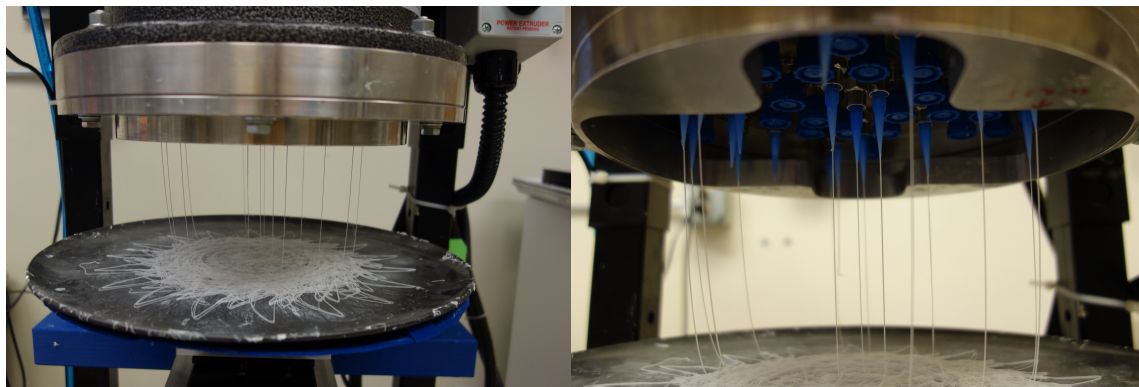
**Figure 4.** Process flow diagram of the lab's pilot-scale demonstration scalable to the target market.<sup>17</sup>

LLNL, in collaborations with industrial partners, plans to increase production of the material on the tons scale with continuous operation within four years of their initial pilot-tests. Within the last year, LLNL has also tested the effects of H<sub>2</sub>S contamination during their 1000-hour operation test. Currently, the team is scaling the test up to 25 kg of composite sorbent in a 30-day campaign at an industrial testing facility—this demonstration would be approximately 1/10<sup>th</sup> of a full-scale operation for small biogas sources such as dairies or food waste digesters.

Through testing, LLNL has successfully found optimal ranges for filament diameter (400-250  $\mu\text{m}$ ), carbonate loading, and hydration percentage.<sup>5</sup> Currently, we are focused on the production of 25 kg of composite sorbent by using a hydraulic extruder paired with an automated moving stage controlled by a computer program (Figure 5). To prepare the PDMS-carbonate composite ink two components, Part A and Part B, are combined and mixed in a FlackTek industrial mixer. The mixture is then filtered through a 440  $\mu\text{m}$  filter to help prevent the nozzles in the hydraulic extruder from clogging.



**Figure 5.** Picture of the hydraulic extruder being used to print a high surface area composite sorbent.



**Figure 6. A close-up picture of the extruder printing a composite sorbent and the number of nozzles used to extrude the material**

Once filtered, a thickening agent is added and mixed to increase the ink viscosity and retain the geometry of the extruded structure. The composite ink is then loaded into the extruder, pushed to the bottom, and put under vacuum overnight. Leaving the material under vacuum overnight allows for some of the air pockets to escape and extrude evenly.

To get the composite sorbents to the required size for the pilot-test, the extrusion process takes around 1-1.5 h per disc of sorbent which is around 28 layers and ranges from 150-200 g. The material is extruded through multiple nozzles while the sample stage at the bottom rotates and moves linearly to obtain a homogenous flat disc (**Figure 6**). PTFE spray is used to coat the sample holder to prevent the composite sorbent from sticking to the tray while the sample is cured in the oven at 110°C for a couple of hours.

### Extrusion Scale-Up

Around 3.3 kg of material can be extruded and cured over 5 days (average 825 g per day) if there is no clogging, and the material is evenly dispersed. The team has currently extruded and cured around 18 kg of material. Since then, we have also started adding more material to the smaller diameter sorbents that were made at the beginning of the project. (**Figure 7**). These smaller diameter sorbents measured anywhere from 14-16 cm in diameter, while the goal is ~18 cm in diameter when dry and 20.3 cm when hydrated. Through hydration tests, we have found that the material swells around 30% of its original size when hydrated to 40%. A Waterjet cut sorbent (17.2 cm diameter) was also hydrated to test swelling (**Figure 7** middle sorbent). The sorbent swelled to 20.3 cm in diameter and was measured to be 60% hydrated, which is not the targeted level of hydration. Therefore, we are planning to cut the dry sorbents to a larger diameter. To ensure all the composite sorbent has the desired diameter, we will use an onsite Waterjet machine to cut the extruded and cured material.

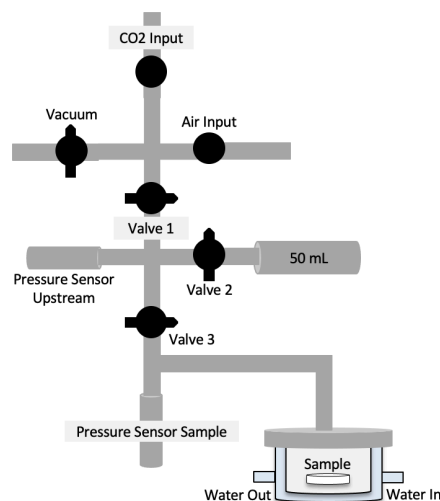
### Pressure Decay Measurements and Results

A simplified schematic of the pressure decay system is shown in **Figure 8**. These pressure decay measurements help us determine the CO<sub>2</sub> absorption capacity, regenerative abilities of the material, and can show the effects of different polymer formulations and geometries. While the thickening agent added to the sorbents increases structural integrity to

the polymer, the team suspected that the thickener may lead to increased leaching of the sodium carbonate, thus leading to lower CO<sub>2</sub> capacity over multiple cycles. Samples with and without the thickening agent were tested.



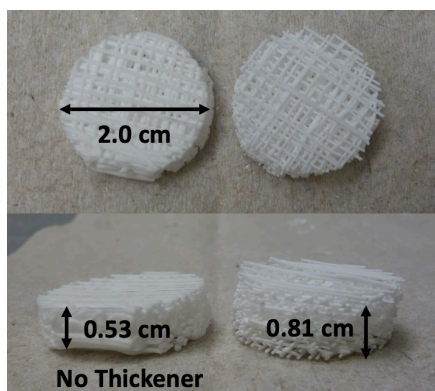
**Figure 7. Three different sizes of extruded and cured sorbents. The goal is to cut the sorbents to a certain size dry, then hydrate them to ~40% to obtain a final 20.3 cm in diameter.**



**Figure 8. Simplified schematic of the pressure decay system and sample holder. The total volume of sample holder and piping after valve 3 is 83 mL.**

Samples were made by hand extruding several layers of the PDMS-carbonate ink into a sheet, curing the material at 110°C for a couple of hours, and then punching out smaller samples using a 2 cm punch hole (**Figure 9**).

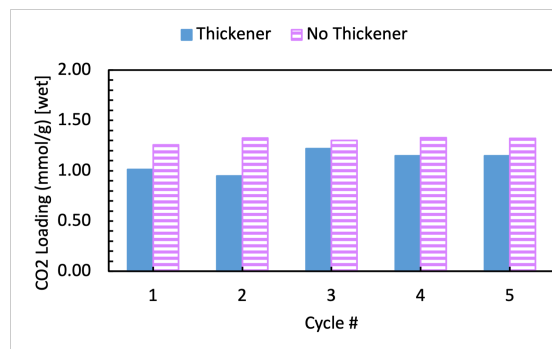
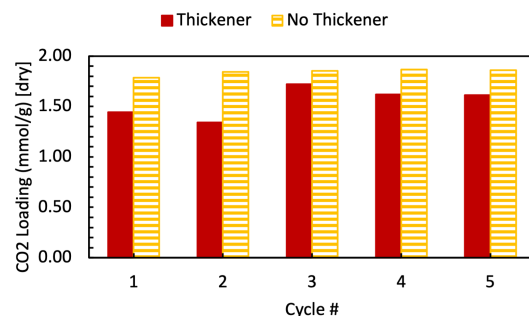




**Figure 9.** Samples hand extruded to the same number of layers and cut out using a 2 cm diameter hold punch. The sample on the left does not contain thickening agent and the sample on the right contains thickening agent. The difference in height between the two samples is apparent.

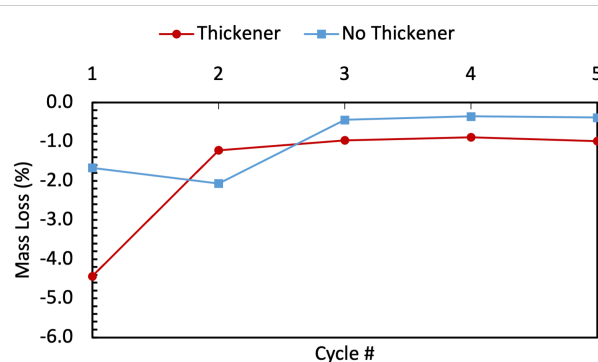
The sample was first hydrated to the desired level in 17 wt% sodium carbonate solution and the volume was measured to track the swelling percentage. Samples with the thickening agent were observed to hydrate significantly faster than the samples without the thickening agent, around 1.3 hours versus 2.75 hours respectively. This difference in hydration times could be due to the hydrophilic properties of the thickener, as well as the increased volume to the samples creating more pores which allows water to disperse through the sample faster. Once hydrated, the sample is washed with DI water and dried with a paper towel to remove any excess sodium carbonate on the surface of the sample.

A typical pressure decay experiment includes: **1)** pulling vacuum on the system to remove any air introduced when setting up the sample; **2)** introducing ~40 kPa of CO<sub>2</sub> to the sample; and **3)** isolating the sample by closing valve 3. The sample is then allowed to absorb the CO<sub>2</sub> and equilibrate for an hour before introducing more CO<sub>2</sub> to equilibrate the sample at 40 kPa. To calculate the total quantity of CO<sub>2</sub> absorbed, the minimum pressure under vacuum, the pressure before CO<sub>2</sub> is introduced, the pressure of CO<sub>2</sub> at the start of the experiment, and the final pressure of CO<sub>2</sub> at the end of each introduction of CO<sub>2</sub> are recorded. The amount of CO<sub>2</sub> absorbed is calculated via the ideal gas law and mass balance. This process is repeated for five cycles regenerating the material by heating in the oven at 110°C. We found there is a slight difference in CO<sub>2</sub> absorption capacity between the samples with the thickening agent and the samples without the thickening agent. The samples with the thickening agent absorbed around 1.1 mol/kg CO<sub>2</sub> while the samples without thickening agent absorbed around 1.3 mol/kg CO<sub>2</sub> (**Figure 10**). The amount of CO<sub>2</sub> absorbed each cycle stayed consistent for both samples. (**Figure 10**).



**Figure 10.** CO<sub>2</sub> loading over five absorption/regeneration cycles per gram of dry material (top) and per gram of hydrated material (bottom).

**Figure 11** shows the mass loss after each regeneration cycle. After the initial first couple cycles, we can see that the mass loss reaches a plateau and levels out by the third cycle. The observation of higher mass loss percentage within cycles 1 and 2 is due to the loss of superficial carbonate that is not encapsulated by the polymer during hydration. I hypothesize that the difference in CO<sub>2</sub> capacity between the two samples is due to this increase in mass loss percentage in the samples with thickening agent (-10% mass loss) compared to samples without the thickening agent (-5.5% mass loss), indicating more loss of sodium carbonate. The different hydrophobic and hydrophilic functional groups of the silicones can lead to higher or lower leaching of the sodium carbonate which, in turn, leads to lower or higher CO<sub>2</sub> absorption over each cycle. Since the thickening agent is hydrophilic, faster hydration occurred but also lead to increased leaching of the carbonate.



**Figure 11.** Mass loss percentage over five absorption/regeneration cycles.



**Figure 12. Finished printed and cured patterns of composite sorbents using different nozzle positions. Different nozzle positions have a significant effect on how the pattern will look in the end. The height of the composite sorbent depends on how many cycles are run.**

### Considerations

Some of the considerations for this project are clogging of the nozzles while extruding which is mostly observed because the material is highly viscous and slowly cures over-time. Clogging can also be caused by the presence of hydroscopic powders in the ink. To prevent nozzle clogging while extruding, the material is filtered using a 400  $\mu\text{m}$  filter before loading into the extruder. Additionally, cured material on the extruder tips can be cleaned between uses. Achieving a homogenous mixture of polymer and powder is crucial for the ease of production and  $\text{CO}_2$  uptake.

The biggest consideration of the project is the shape and pattern of the printed sorbent. **Figure 12** shows the difference between nozzle patterns and number of cycles. The goal is to make the composite sorbents flat and uniform so they can be easily stacked in a column. Depending on how the nozzles are set and material distributed in the extruder, we have trouble achieving the uniform disc. For the example, we have a particular difficulty with the extruded part doming in the middle which decreases the stacking ability. After testing multiple nozzle settings, we have now found the best nozzle arrangement to increase the uniformity and make the outer part of the composite thicker. Even after finding a more suitable nozzle setting, the whole process is not entirely automatic. If we truly want a uniform disc, one must monitor the printing process and occasionally open and close nozzles as needed.

This process become more time-intensive if the material is not evenly distributed in the extruder or if clogging is a constant issue. Additionally, we still must manually change the sample tray every hour or so depending on the desired thickness or uniformity of the sample. Because we must switch out nozzles and change the pattern to compensate for areas lacking or having excess material, predicting if the sorbent will be print flat is difficult. Fortunately, after curing the printed structure, we can add more material on top if needed and is the current focus of the project.

### Risk Management

Other considerations include commercial and technical risks which can compound during the scale-up. One of the commercial risks includes the development cycle being too slow and the small-scale biogas market will be saturated in the next 3-5 years. LLNL plans to mitigate this by discussing with stakeholders, continuing to assess technology needs, and pivoting, if necessary, to a different market.<sup>17</sup>

Technically, the sorbent material hydration levels are difficult to maintain if the source biogas or regeneration gas is not an appropriate humidity level. Hygrometers can be placed on the reactor to monitor reactor bed humidity and the blower air can also be hydrated. Additionally,  $\text{H}_2\text{S}$  contamination is a concern for most biogas upgrading technologies but, LLNL does not foresee  $\text{H}_2\text{S}$  contamination causing the sorbents to fail. They expect the  $\text{H}_2\text{S}$  will concentrate in the carbonate phase and be removed during regeneration but will plan to implement  $\text{H}_2\text{S}$  purification upstream if needed. Lastly, the lab predicts there may be sorbent martial instability over cycling which can be mitigated by decreasing the particle size, modifying the amount and identity of silica filler in polymer, or identifying process modifications that might alleviate instability.<sup>17</sup>

### PROJECT SCOPE – CONFINED COAXIAL POWDER EXTRUSION

In continuation to LLNL's advanced manufacturing  $\text{CO}_2$  sorbent materials, the team proposed to develop a confined coaxial powder extrusion (CCAPE) to increase the carbonate loading within these composite materials. LLNL wishes to develop a coaxial nozzle and demonstrate extrusion of a carbonate powder core encased in a silicone shell. Because these unique materials capture  $\text{CO}_2$  as a bicarbonate solution, increasing the carbonate loading also increases surface area for solution-gas interactions enabling the higher  $\text{CO}_2$  loading. Additionally, during the development of the composites, there is an initial mass loss of carbonate within the first few cycles of absorption and regeneration due to the loss of superficial carbonate not encapsulated by the polymer.

If too much sodium carbonate is leached from these materials, the overall CO<sub>2</sub> capacity also decreases. The goal of this project is to develop a method of confining solid carbonate powders within a CO<sub>2</sub> permeable silicone sheath to enable high loading CO<sub>2</sub> sorbent materials and reach economic targets and rapid mass transport in materials based on solid sorbents. LLNL hopes to use vibrational assisted powder extrusion (VAPE) to achieve a flowable powder into a vessel of any shape. The advantages of these materials over the composite sorbents include high loading of solid sorbents, doubling the CO<sub>2</sub> capacity, minimizing material leaching, and potential shaping using a 3D printer. If successful, this technique can also be applied to other solid sorbents that require structural support such as metal organic frameworks (MOFs). Additionally, these materials would be competitive with other direct air capture methods such as solid sorbent pelletization which requires other chemical binders, immobilization of the sorbents onto porous substrates, and are limited by surface area and functionalization techniques.

### Considerations

To ensure the success of encasement, we must find a proper polymer mixture that has a viscosity that will print but also hold its shape around the powder and is CO<sub>2</sub> permeable. If the polymer viscosity is too low, then the printed filament will not hold shape causing the polymer shell to break and the powder to leach out. On the other hand, if the polymer viscosity is too high, printing a thin polymer shell will be difficult to do with the pressure limitations that we face potentially causing the shell to be too thick.

Next, exploring the effect of core-to-shell thickness ratio will determine the amount of CO<sub>2</sub> absorbed and structural integrity of the sample. Again, if the shell is too thin, then there is high probability the polymer shell will rupture, and the powder will leach. If the shell is too thick, the longer the hydration process as well as increased chances the powder will not have complete dissolution.

### Risk Management

Other concerns and anticipated challenges for CCAPE include mass-transfer limitations and structural integrity of the polymer shell once hydrated. To avoid mass-transfer limitations, the diameter of the powder core must be a certain size which could significantly impact the CCAPE nozzle design especially when using hygroscopic powders. Our goal is to find the optimal shell to core ratio to achieve the highest CO<sub>2</sub> absorption with good structural integrity. We can also attempt to mill, sieve, and store the powder in a desiccator to reduce agglomeration and increase particle uniformity. Additionally, once we hydrate these samples, we want to make sure that the polymer shell will also expand and flex to accommodate the densely packed powder core. The polymer shell could either rupture or not allow for complete dissolution of the carbonate. Mitigation includes finding the optimal polymer formulation that would allow for expansion and dissolution of the powder core.

## FUTURE DIRECTIONS AND CONCLUSIONS

With the upscale of the composite sorbents occurring, the team is also working to refine these silicone-carbonate materials. Again, these materials are of high interest due their water compatibility, easy regeneration, stability over many cycles, low toxicity, and cost compared to other gas scrubbing methods. With the ability to produce pipeline quality biomethane, LLNL is moving to do a test at a kilogram scale. Current production is underway with almost 15 kg of material extruded and cured. The group is constantly fine-tuning and adjusting the current nozzle patterns to achieve uniform and stackable composite sorbents. A recent techno-economic analysis revealed that the CO<sub>2</sub> absorption capacity must be at least double the current absorption capacity to ensure a competitive technology. Unfortunately, increasing the CO<sub>2</sub> absorption capacity is not as simple as increasing the carbonate loading. LLNL has found, with the current formulation, increasing the carbonate loading results in lower absorption capacities. For this reason, we are currently exploring alternative options such as CCAPE.

LLNL continues to look to the future of these materials by increasing CO<sub>2</sub> absorption capacity using co-axial powder extrusion. Future work includes optimizing the powder core-to-shell ratio, finding the optimal polymer formulation to allow for expansion and complete dissolution of the powder core, and running pressure decay tests to measure CO<sub>2</sub> absorption. These materials also have potential to be printed into different 3D structures.

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