

New Sky Energy, LLC

CCEMC Grand Challenge Project ID: K130125

<u>Round 1 Final Outcomes Report</u>: Soda Ash and Bicarbonate from a Low Energy Natural Gas Sweetening Process

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# **Executive Summary**

**Background:** Alberta is a leading global producer of natural gas, which is an affordable, lowcarbon fossil fuel. However, as much as one-third of Alberta's gas production has historically been sour gas, containing large amounts of carbon dioxide ( $CO_2$ ) and hydrogen sulfide ( $H_2S$ ), and as a result, producing lower energy value and much higher direct and indirect lifecycle  $CO_2$ emissions than sweet gas. Due to these undesirable characteristics large reserves of sour natural gas remain untapped in Alberta. If such reserves could be economically and sustainably treated it would enable Alberta to lead a far more rapid global transition from coal to natural gas power and establish the province as a major clean energy leader.

In 2014 New Sky Energy was awarded a \$500,000 CAD grant from CCEMC to demonstrate and develop an energy efficient gas sweetening strategy that removes hydrogen sulfide and CO<sub>2</sub> from sour natural gas and mineralizes the CO<sub>2</sub> to form commercially valuable carbonates such as soda ash and sodium bicarbonate. Conventional processes to sweeten sour gas and produce carbonates are expensive, energetically wasteful and create substantial GHG emissions. The New Sky gas sweetening process relies on two technologies invented and commercialized by New Sky; SulfurCycle E, which captures and converts H<sub>2</sub>S into sulfur and hydrogen, and CarbonCycle, which converts CO<sub>2</sub> and sodium sulfate, an abundant, low cost natural salt, into sodium hydroxide, carbonates, hydrogen and sulfuric acid. Together these technologies provide a low cost, energy efficient, highly sustainable strategy to sweeten sour natural gas and create multiple high value products from the waste hydrogen sulfide and CO<sub>2</sub>.

**Progress:** In the two years since receiving CCEMC grant money New Sky has achieved the following technical and business milestones:

- Optimized CarbonCycle and SulfurCycle E chemistries in the company's Boulder CO laboratories. Both chemistries performed as expected, with dramatic energy savings observed when sodium sulfide (the product of gas sweetening to remove H<sub>2</sub>S) was electrolyzed in a SulfurCycle reactor
- Piloted CO<sub>2</sub> capture/mineralization and SulfurCycle E electrochemistry at a large natural gas field in Oklahoma, treating 30,000 SCF of sour natural gas per day. Both SulfurCycle electrochemistry and NaOH based capture of H<sub>2</sub>S and CO<sub>2</sub> performed as expected
- Piloted CO<sub>2</sub> capture and mineralization to form soda ash and bicarbonate at Avery Brewing, a world-class craft brewery in Boulder CO. Two-liter and 200-liter scrubbers were used to generate high quality soda ash and sodium bicarbonate
- Invented, optimized and patented SulfurCycle R, a gas sweetening technology that selectively removes H<sub>2</sub>S but not CO<sub>2</sub> from gas streams. The remaining stream of natural

gas and  $CO_2$  can be treated with NaOH (produced by CarbonCycle or SulfurCycle E) to create sweet gas and carbonates for market

- Signed multi-million dollar licenses for use of SulfurCycle E and R in US oil and gas markets and received \$3.5M USD in royalty and revenue payments for use of these technologies in the United States
- Successfully piloted SulfurCycle R at municipal wastewater treatment plants in Colorado and Los Angeles, treating 75,000 SCF of sour bio-methane per day
- Commercially deployed SulfurCycle R at a natural gas field in SW Wyoming in March 2016, initially treating 300,000 SCFD of sour natural gas.
- Sold and deployed a second commercial gas sweetening system in Wyoming, which is scheduled to begin treating 1 million SCFD of sour gas in May 2016
- Established a hundred-fold range of CO<sub>2</sub> to H<sub>2</sub>S ratios (1:10 to 10:1) that "work" effectively for New Sky gas sweetening and CO<sub>2</sub> mineralization. The great majority of sour gas fields in Alberta fall within this broad range of CO<sub>2</sub>:H<sub>2</sub>S ratios
- With support from US energy industry partners and CCEMC funding New Sky more than doubled its staff, adding ten chemists, chemical engineers and machinists.
- In advanced negotiations to sell biogas sweetening systems to wastewater treatment plants in Colorado, Washington and British Columbia
- Developed plans to deploy SulfurCycle and CarbonCycle technologies in Canada and signed a Letter of Intent with Alberta-based Imaginea Energy
- Attended Globe 2016 conference in Vancouver BC and established business connections likely to lead to commercial gas sweetening projects in Alberta and British Columbia, as well as other projects in the US

Having received CCEMC Round One funding in the spring of 2014, New Sky set out to demonstrate its novel, low energy strategy to sweeten natural gas and mineralize  $CO_2$ . Two years later we have accomplished everything we set out to do. In a series of successful pilot and laboratory projects in Oklahoma and Colorado, New Sky used its SulfurCycle E process to efficiently capture H<sub>2</sub>S and CO<sub>2</sub>, mineralize the CO<sub>2</sub> into valuable carbonates, and produce carbon neutral hydrogen as a bonus. The great majority of sour natural gas in Alberta--trillions of cubic feet of gas--is well suited to treatment with the New Sky process, generally at prices well below current gas sweetening costs.

# Introduction and Project Overview

### Background: An Ideal CO<sub>2</sub> Mineralization Strategy for Alberta

New Sky Energy was founded in 2007 to develop and commercialize CarbonCycle, a carbon negative manufacturing strategy that captures and mineralizes  $CO_2$  without producing by-product chlorine. New Sky and other companies that mineralize  $CO_2$  generally rely on sodium hydroxide (NaOH), a strong base that reacts with acid gases such as  $CO_2$ ,  $SO_x$  and  $H_2S$ . Conventional strategies for manufacturing sodium hydroxide are energy intensive and produce large amounts of by-product chlorine, a toxic, volatile chemical that was widely used as a World War I trench gas. Chlorine has an IDLH (Immediately Dangerous to Life and Health) concentration of 10 ppm. Trading  $CO_2$  for chlorine gas is a bad idea.

To avoid chlorine production, New Sky patented the company's CarbonCycle Process, a novel strategy of water splitting that uses sodium sulfate to generate NaOH and sulfuric acid. Sodium sulfate is an abundant natural salt, particularly in Alberta and Saskatchewan, and also a common industrial waste product known as salt cake. Sulfuric acid is the world's largest commodity chemical and can be used to digest cellulose to form simple sugars for production of CO<sub>2</sub> neutral biofuels and biopolymers. This duel strategy--avoiding chlorine and generating a non-toxic sulfuric acid byproduct with potentially enormous, low carbon markets of its own--is the reason that we believe New Sky's CarbonCycle process will ultimately prevail as the most sustainable and cost-effective pathway to generate sodium hydroxide for CO<sub>2</sub> mineralization.

Having successfully developed and patented CarbonCycle in the US, Canada, China and Australia New Sky turned its attention to gas sweetening and hydrogen sulfide capture. Hydrogen sulfide is a high toxic chemical that must be removed from sour natural gas, biogas and many other industrial gas streams. Fortunately H<sub>2</sub>S contains significant potential energy as a chemical reducing agent and serves as a source of CO<sub>2</sub>-neutral hydrogen. New Sky scientists saw a significant opportunity to exploit hydrogen sulfide as a useful chemical and energy resource and this became the basis of the company's SulfurCycle E technology.

The reaction of  $H_2S$  with sodium hydroxide creates sodium sulfide (Na<sub>2</sub>S) and sodium bisulfide (NaSH). Concentrated solutions of these sulfides can contribute energy and electrons in an electrochemical cell, effectively acting like battery electrolytes. This contribution of energy creates the potential to dramatically reduce the energy cost of sodium hydroxide production, which in turn reduces the energy and CO<sub>2</sub> emissions associated with gas sweetening and CO<sub>2</sub> mineralization.

At the anode, SulfurCycle E reactors convert sodium sulfide into sulfur and polysulfides; at the cathode the reactor produces sodium hydroxide and hydrogen. The contribution of energy and electrons from sulfide ions at the anode reduces the minimum voltage potential for sodium hydroxide formation from 2.06V to 0.43V, a remarkable improvement in energy efficiency. Since sodium sulfide is the byproduct of gas sweetening to remove H<sub>2</sub>S its use in SulfurCycle E

reactors represents a novel, low energy strategy to sweeten gas, regenerate sodium hydroxide and convert  $H_2S$  into hydrogen and sulfur. Any sodium hydroxide that instead reacts with  $CO_2$  forms valuable carbonates for market.

During New Sky's Oklahoma gas sweetening project, New Sky scientists conceived of a novel, highly sustainable strategy to separate H<sub>2</sub>S from CO<sub>2</sub> and methane in sour natural gas or biogas streams. This process, SulfurCycle R, utilizes a safe, low cost suspension of metal oxide nanoparticles in water to react with hydrogen sulfide in sour gas, temporarily forming a metal sulfide suspension. When the metal oxide suspension is completely or partially spent (i.e., converted to metal sulfide) it can be fully regenerated by exposure to air, which oxidizes the metal sulfide to elemental sulfur and regenerated metal oxide. Eighteen months after initial experiments confirming the process chemistry New Sky commercially deployed SulfurCycle R at a sour natural gas field in SW Wyoming.



Skid mounted SulfurCycle R gas sweetening system (center) at a sour natural gas field near Rock Springs, Wyoming, May 2016. Sour natural gas enters the base of the scrubber column and rises through a water based metal oxide suspension. H<sub>2</sub>S reacts with the metal oxide and is converted to metal sulfide; pipeline spec gas (< 4 PPM H<sub>2</sub>S) emerges from the column. Spent media is regenerated by exposure to air in a smaller column located in a nearby building (far right) to protect the media from cold weather. SulfurCycle R can treat gas streams containing 10 PPM to 50,000 PPM of hydrogen sulfide.

SulfurCycle R specifically captures H<sub>2</sub>S but not CO<sub>2</sub> from gas streams, and is useful in sweetening a wide variety of gas streams that are not immediately suited to SulfurCycle E and CarbonCycle processing. For example, many sour gas streams contain small amounts of H<sub>2</sub>S and higher levels of CO<sub>2</sub>. For safety and regulatory reasons the H<sub>2</sub>S must still be removed, but its levels may be too low to support cost effective SulfurCycle E operations. SulfurCycle R can treat such low H<sub>2</sub>S gas streams to produce H<sub>2</sub>S-free gas that contains varying levels of CO<sub>2</sub>. The carbon dioxide contained in these gas streams can then be captured by sodium hydroxide produced by CarbonCycle or SulfurCycle E, producing pure, sulfide-free carbonates for market.

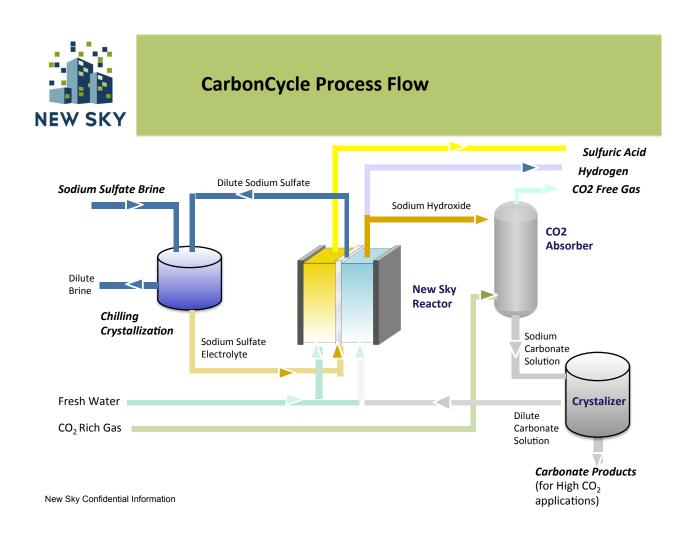
CarbonCycle, SulfurCycle E and SulfurCycle R can be deployed in various configurations to treat a variety of sour gas streams at complex gas fields. Individual wells at sour gas fields frequently have very different gas compositions, and selective use of New Sky's gas sweetening technologies would allow operators to create gas mixtures that are ideal for cost effective gas sweetening and CO<sub>2</sub> mineralization.

The following pages contain process flow diagrams illustrating SulfurCycle E, CarbonCycle and SulfurCycle R.

When used in combination, CarbonCycle, SulfurCycle E and SulfurCycle R create profitable, highly sustainable strategies to sweeten sour natural gas or biogas and produce carbon neutral carbonates and hydrogen gas. This promising strategy was the basis of New Sky's 2014 CCEMC grant, and two years later we are happy to report that the strategy, through multiple pilots and lab experiments, has worked exactly as expected.

The rest of this final report summarizes the work that we have completed under our Round 1 CCEMC grant, its conclusions and their economic and environmental relevance to the province of Alberta, and proposed next steps to commercially deploy New Sky's gas sweetening and CO2 mineralization technologies in Canada and globally.

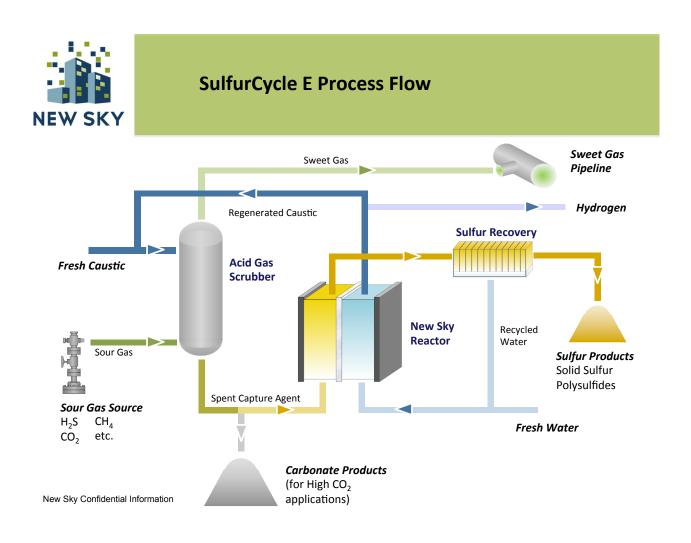
# New Sky Technologies – Process Flow Charts



**New Sky's CarbonCycle Process** is a an energy efficient electrochemical process that converts sodium sulfate and carbon dioxide into sodium carbonate, sodium bicarbonate, sodium hydroxide, hydrogen, oxygen and sulfuric acid. Using renewable or other low carbon electricity, CarbonCycle carbonates are  $CO_2$  negative, incorporating more carbon dioxide than is produced during their manufacture.

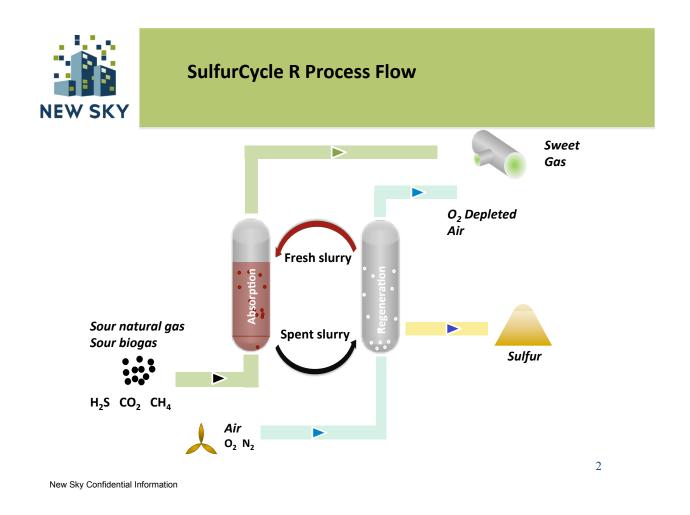
CarbonCycle's input salt, sodium sulfate, is a common industrial waste salt and an abundant natural resource in Alberta and Saskatchewan. CarbonCycle thus provides an excellent strategy for Canadian companies to convert a low cost natural resource and waste  $CO_2$  into valuable carbon negative chemicals. Unlike conventional chloralkali process CarbonCycle does not produce by-product chlorine, an important advantage in large scale  $CO_2$  mineralization strategies. CarbonCycle can serve as the source of sodium hydroxide for use in SulfurCycle E gas sweetening.

The CarbonCycle Process (US Patent 8,227,127) is patented in the US, Canada, China and Australia.



**SulfurCycle E** is an energy efficient gas sweetening process that converts  $CO_2$  into useful carbonates and hydrogen sulfide (H<sub>2</sub>S) into elemental sulfur. SulfurCycle E utilizes sodium hydroxide, a CarbonCycle chemical output, as the capture agent for  $CO_2$  and H<sub>2</sub>S. Sodium sulfide, the H<sub>2</sub>S capture product, is converted in a SulfurCycle electrochemical reactor into hydrogen gas and sodium hydroxide, which is available for additional sour gas processing.

SulfurCycle E takes advantage of the inherent chemical energy of the sulfide ion to reduce the theoretical minimum voltage required to generate sodium hydroxide from 2.06V to just 0.43V, nearly an 80% energy savings. Effectively the sulfide capture solution acts like a battery electrolyte. SulfurCycle E is the most energy efficient process known for conversion of hydrogen sulfide into hydrogen gas and sulfur. With SulfurCycle E, waste hydrogen sulfide from sour natural gas or biogas represents a carbon free source of hydrogen gas, offering additional GHG benefits beyond the conversion of CO<sub>2</sub> to carbonates.



**SulfurCycle R** is New Sky's highly sustainable, low cost method of selectively removing hydrogen sulfide from sour natural gas and biogas. SulfurCycle R utilizes a water-based suspension of a low cost metal oxide reagent to capture and convert hydrogen sulfide into elemental sulfur. Invented during New Sky's CCEMC pilot project in western Oklahoma in November 2014, New Sky fully commercialized SulfurCycle R within 18 months, and now operates a 1 MMCFD gas sweetening plant in SW Wyoming.

SulfurCycle R provides an excellent method of separating hydrogen sulfide from  $CO_2$  in sour natural gas and biogas. This characteristic allows fine-tuning of sour gas streams to achieve optimal  $H_2S$  to  $CO_2$ ratios for energy efficient production of carbonates from  $CO_2$  utilizing SulfurCycle E and CarbonCycle.

# **Project Goals**

	Goal	Achievement
1.	Identify an Alberta based energy company partner (execute a pilot agreement with an Alberta-based energy industry partner)	<ul> <li>New Sky partnered with a US oil an gas company to pilot its SulfurCycle E technology at a sour natural gas field in western Oklahoma. In 2016 New Sky signed a Letter of Intent with Alberta-based Imaginea Energ to deploy its SulfurCycle technolog during Round 2 of the CCEMC Gran Challenge, if New Sky is selected. We are seeking other Alberta energy industry partners as well</li> </ul>
2.	Scale up all processes by 20-50x	<ul> <li>Completed.</li> </ul>
3.		Completed.
4.	Generate engineering designs for a 50 MCF/day gas sweetening/ CO2 mineralization pilot.	<ul> <li>Completed. The OK pilot utilized a 50 MCF/day slipstream from a 300 MCF/day well.</li> </ul>
5.	-	<ul> <li>Treated 50 MCF/day of sour gas, producing and selling pipeline quality gas for two weeks in November 2014</li> </ul>
6.	Capture and convert up to 100 kg of CO <sub>2</sub> per day into 200+ kg of high quality anhydrous soda ash or bicarbonate for sale to Verallia and other interested buyers	<ul> <li>Captured hundreds of kilograms of CO<sub>2</sub> and H<sub>2</sub>S in Oklahoma and Colorado pilot projects and Wyoming commercial scale SulfurCycle operations</li> </ul>
7.	Achieve profitable sour gas sweetening	<ul> <li>In early 2016, New Sky permanentl installed and began operating a SulfurCycle plant in Wyoming. To- date, this plant has operated at a cost below the conventional MEA</li> </ul>

triazine system in use previously, and at a cost sufficient to earn a profit on gas sold at \$2/MCF

# **Project Final Outcomes**

# Desulfurization of Sour Gas, Regeneration of NaOH & Capture of CO<sub>2</sub>

After significant laboratory and engineering progress toward scale up of the company's energy efficient SulfurCycle E gas sweetening/carbon dioxide mineralization process, New Sky conducted a large-scale field pilot in western Oklahoma in late 2014. During this pilot, we successfully demonstrated all SulfurCycle E process steps, producing pipeline quality natural gas, industrially useful carbonates and sulfur.

After installation, each subsystem of the SulfurCycle E technology was commissioned using high-pressure sour gas and corrosive process chemicals. On November 5, 2014, New Sky completed its first operational run of the gas scrubber system. New Sky later made in-field modifications to the scrubbing and capture solution treatment systems, including adding a dewpoint control system, heating cable and insulation for the scrubber, and an additional filter for the gas capture treatment.

On November 14<sup>th</sup> 2014, New Sky operated the electrochemistry system using commercial sodium sulfide as electrolyte. The commissioning phase of the project culminated with a full demonstration of the complete, closed-loop process.



Left: New Sky SulfurCycle E pilot project near Woodward OK, November 2014. The tall scrubber column at left side of the pilot skid contains a sodium hydroxide solution, used to sweeten up to 30MCF/day of sour natural gas containing approximately 7000 ppm of CO<sub>2</sub> and 350 ppm of H<sub>2</sub>S. Virtually all CO<sub>2</sub> and H<sub>2</sub>S were removed after treatment. Sodium sulfide salts in the spent capture solution were electrochemically regenerated in New Sky's SulfurCycle E reactor.

During pilot operations, New Sky successfully sweetened a significant slip-stream (up to 30 CFM out of 200 CFM) of the natural gas from the existing sour gas line upstream of existing gas sweetening equipment. The diverted sour gas was bubbled through a New Sky scrubber column containing sodium hydroxide solution to remove H<sub>2</sub>S and CO<sub>2</sub>, and the sweetened natural gas was returned to the sales pipeline. The captured H<sub>2</sub>S and CO<sub>2</sub>, then in the form of sodium sulfide and sodium carbonate, were treated to remove undesirable organics and particulates. The resulting clean capture solution was electrolyzed in a SulfurCycle E reactor to

regenerate sodium hydroxide and convert sulfide to sulfur. The remaining brine was rich in sodium carbonate (>15% w/vol), which was then recovered as crystalline sodium carbonate decahydrate by chilling the solution. In total, approximately 100 pounds (45 Kg) of sodium carbonate was recovered from the Oklahoma pilot well.

The raw natural gas in our Oklahoma test well contained approximately 7,000 ppm of CO<sub>2</sub> and 350 ppm of H<sub>2</sub>S. After treatment these acid gases had been reduced to trace levels <4 ppm), with the resulting sweetened natural gas suitable for sale as pipeline quality gas. The post treatment H<sub>2</sub>S level in the sweetened gas was typically at 0.1 - 2 ppm, well below the 4-ppm limit allowed in most commercial natural gas pipelines. As a key part of the onsite pilot activities, New Sky regenerated spent sodium hydroxide capture agent using a SulfurCycle E electrochemical reactor, closing the capture loop at much lower energy, cost and CO<sub>2</sub> footprint than buying conventionally manufactured sodium hydroxide. In addition, SulfurCycle E's regeneration step produced hydrogen gas, which increased the BTU value of the natural gas in direct proportion to its original H<sub>2</sub>S concentration.

New Sky's Oklahoma field pilot and subsequent laboratory research confirmed that SulfurCycle E efficiently removes both H<sub>2</sub>S and CO<sub>2</sub> from natural gas streams, producing pipeline quality natural gas, carbonates and sulfur. In the pilot test, up to 30,000 scf of natural gas per day containing significant levels of CO<sub>2</sub> and H<sub>2</sub>S was scrubbed with a sodium hydroxide solution in a fluid filled bubble column (see photo). The scrubbing process generated a concentrated sodium carbonate/sodium sulfide solution, which we electrochemically processed in a SulfurCycle E reactor to regenerate sodium hydroxide from the sulfide salt. The remaining sodium carbonate



SulfurCycle E reactor at New Sky Oklahoma pilot project, November 2014. The reactor efficiently converted sodium sulfide, captured as  $H_2S$  from sour natural gas, into hydrogen, sulfur and sodium hydroxide.

solution, largely sulfide-free, was then further processed to precipitate sodium carbonate, which was then recrystallized and dried to produce high quality dense soda ash suitable for glass manufacturing.

New Sky's Oklahoma pilot project convincingly demonstrated the feasibility of using the chemical energy of captured hydrogen sulfide to mineralize  $CO_2$  via a sustainable, low energy pathway. New Sky's process simultaneously captured  $H_2S$  and  $CO_2$  from sour natural gas and then used a SulfurCycle reactor to regenerate the sodium hydroxide capture agent at a fraction of the energy cost of conventional NaOH manufacturing. Overall the process produced sweet natural gas, hydrogen, sulfur and marketable carbonates made from the captured  $CO_2$ .

# Mineralization of Carbonate Solutions

Sodium hydroxide is a powerful caustic reagent that readily captures  $CO_2$  from gas streams and converts it into sodium carbonate. To capture and mineralize  $CO_2$ , New Sky researchers tested fluid filled bubble columns, packed beds and falling film contactors. All of these approaches were efficient and simple to operate, and proved to be reliable  $CO_2$  capture strategies. However, the reaction of  $CO_2$  with caustic solutions is just the beginning of soda ash mineralization process, and conversion of these solutions into solid soda ash or sodium bicarbonate is critical to carbonate commercialization.

The desired final carbonate product and its quality specifications can affect the choice of capture equipment and operating procedures as well as the hand off of raw solutions to mineralization equipment. By integrating capture and mineralization, New Sky was able to produce dense soda ash, sodium carbonate decahydrate, sodium bicarbonate and precipitated calcium carbonate from CO<sub>2</sub> captured in field site gas scrubbing operations.



New Sky mineralized carbonates produced from CO<sub>2</sub>.

# Soda Ash

Soda ash is traditionally produced in a thermal evaporative crystallizer from a solution of sodium carbonate. The solution is subjected to evaporation at elevated temperatures between 40°C and 100°C in order to concentrate the liquor beyond its saturation point, thereby forming sodium carbonate monohydrate crystals. These crystals are dewatered, dried and sized to produce anhydrous soda ash<sup>(1-2)</sup>.

**Preparing a stock solution:** Based on this simplified description of soda ash production, one may conclude that generating saturated sodium carbonate solutions facilitates crystallization and lowers energy demand. However, absorbers are challenged by saturated carbonate

solutions, which form precipitates that clog aerators, seize pumps and affect fluid dynamics. To further complicate the process, sodium carbonate solutions are very temperature sensitive, with low solubility at low temperatures (<1.0M below 10°C), and much higher solubility at warm temperatures (>4.0M above 35°C). Hence it is critical to operate CO<sub>2</sub> contactors at a concentration slightly below their saturation point at a given contact temperature, to optimize the concentration of the carbonate solution.

In New Sky's field pilots, all contactors were operated near 20°C. Sodium hydroxide was typically provided at  $\leq$ 4M to produce  $\leq$ 2M sodium carbonate, according to the formula:

 $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$ 

This final sodium carbonate concentration is low enough to prevent crystallization in the contact equipment at 20°C. Carbonate solutions produced off-site were transported to New Sky and crystalized at higher temperatures to form sodium carbonate monohydrate, which was harvested and dried to form dense soda ash. Ideally in future industrial deployments, the contactor and crystallizer will work together under steady state conditions that maintain optimal NaOH concentrations (near 4.0M) and temperature (>40°C) to minimize energy demand for thermal evaporation.

At New Sky's Oklahoma sour gas field site, sodium carbonate solutions freshly generated from CO<sub>2</sub> captured at the wellhead were chilled to precipitate sodium carbonate decahydrate, thus removing a great deal of the water (~50%) from the carbonate product. This "cold concentration method" relies on the unusual precipitation characteristics of sodium carbonate solutions and uses 10x less energy to remove excess water than thermal evaporation. When warmed, the resulting sodium carbonate product dissolves and at temperatures above 35°C essentially becomes a saturated (~4.0M) solution of sodium carbonate monohydrate. The resulting solution is ideal for dense soda ash production using conventional techniques used in the soda ash industry.

The energy efficient processes used to produce conventional soda ash from trona ore result in production of 411 kg of CO<sub>2</sub> per ton of soda ash. However the release of CO<sub>2</sub> when conventional soda ash is calcined during glass manufacturing results in release of an additional 415 Kg of CO<sub>2</sub> per ton of soda ash. New Sky's soda ash contains CO<sub>2</sub> captured from sour natural gas. Most of the CO<sub>2</sub> contained in Alberta's sour gas is released to the air during natural gas combustion or sour gas sweetening processes. New Sky's SulfurCycle E process captures that CO<sub>2</sub> and forms a carbon neutral soda ash, hence avoiding the release of 415 Kg of CO<sub>2</sub> per ton when our soda ash is used in glass manufacturing. In effect conventional gas sweetening and soda ash production/use release two CO<sub>2</sub> molecules, one from fossil fuel (sour gas) and one from "fossil carbonate" (trona), whereas New Sky's process releases just one: the CO<sub>2</sub> captured from sour natural gas that is used to make New Sky soda ash.

**Pretreatment:** Since sodium hydroxide is such a powerful caustic reagent, it also reacts strongly with hydrogen sulfide ( $H_2S$ ), which is typically co-produced with  $CO_2$  in sour natural gas and

biogas. The cold precipitation mentioned above has the added benefit of separating precipitated carbonates from dissolved sulfides. A single precipitation removes the majority of the sulfides (>98%) from the raw carbonates leaving a preferred high sulfide/low carbonate electrolyte for SulfurCycle E and a much cleaner carbonate product. However, the odor threshold of sulfides is well below 1 ppm, so several strategies were considered to remove the remaining sulfides from the carbonate prior to thermal evaporative crystallization.

One strategy involves multiple cold crystallizations of sodium carbonate decahydrate. Although effective, the energy demand is high and best suited for initial bulk separation of carbonates and sulfides. Once sulfides are at concentrations below 100 ppm, treating with metal ions such as iron, zinc or barium salts is an effective approach. New Sky's SulfurCycle R chemistry can also be used to remove trace levels of hydrogen sulfide from gas and liquid streams. When added to a carbonate solution containing low levels of sulfide the SulfurCycle R capture media reacts with sulfides and precipitates iron sulfide, effectively removing the trace H<sub>2</sub>S from the carbonate solution. SulfurCycle R can also be used upstream of the NaOH capture solution, separating H<sub>2</sub>S and CO<sub>2</sub> capture into separate steps. This approach makes sense if levels of H<sub>2</sub>S are too low to offer significant energy benefits when electrolyzed in SulfurCycle E reactors. The resulting desulfurized gas stream can be scrubbed with New Sky NaOH (produced by CarbonCycle or SulfurCycle E), creating pure sodium carbonate solutions and sweet natural gas.

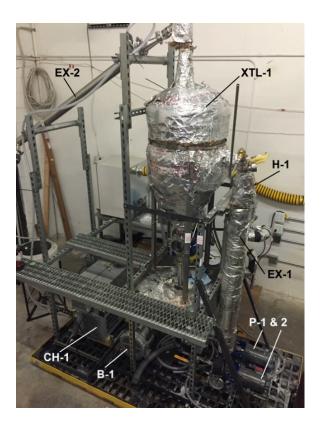
**Crystallizer:** By applying knowhow from previous field projects, New Sky designed and built a soda ash crystallizer which incorporated the following key design criteria:

- A mechanism to supersaturate the solution (evaporate water)
- A mechanism to capture steam (condenser)
- A mechanism to nucleate and grow crystals from super-saturated solutions
- Indirect heating
- Forced circulation
- A mechanism to facilitate mass transfer (air flow to carry away steam)
- A mechanism to harvest crystal carbonate products

After review of the many known crystallizer systems, New Sky chose to build a forced circulation crystallizer based on the Swenson design<sup>(3-4)</sup>. The photo below shows the key design features and equipment. This small demonstration crystallizer is very inefficient compared to the industrial scale equipment used in conventional soda ash production, which have sophisticated heat recovery systems. In large-scale soda ash production New Sky would adopt the most energy efficient crystallization and drying processes, matching or improving on the best practices of the industry. This strategy will maximize the GHG benefits of our  $CO_2$  capture process.

A life cycle assessment of GHG emissions during conventional soda ash production indicates that approximately 410 Kg of CO<sub>2</sub> is generated during production of one ton of dry soda ash. An additional 415 Kg of CO<sub>2</sub> is emitted during calcination of conventional soda ash in a glass

furnace. <sup>(5)</sup> New Sky's process has the potential to reduce soda ash emissions by 415 Kg, since  $CO_2$  released during calcination was effectively an avoided  $CO_2$  emission during gas sweetening.



# *New Sky crystallizer configured for standard operation.*

This image shows a small soda ash crystallizer with key equipment labeled. All hot equipment required insulation to avoid thermal losses due to a relatively large  $\Delta T$  between ambient and steady state temperature (~70°C). The system also benefited from the airflow provided by the blower which allowed the system to operate at 70°C rather than 90°C. The blower increased mass transfer and reduced demand on the condenser. Not shown is the tangential entry of the working liquor to allow longer residence in the crystal growth chamber of the crystallizer. Sodium carbonate monohydrate crystals require post processing to produce dense soda ash. The first challenge involved removing crystals from the reactor. To simplify the system, the crystallizer was run in a batch mode until sufficient product was produced. The crystals were immediately removed through a low point drain while still hot and allowed to settle in a tank to decant the excess liquor and vacuum filter to remove excess water. The monohydrate crystals were then dried in an oven at >102°C to produce soda ash. Steady state continuous processes typically employ in-line particle removal, hydro-cyclones for dewatering and rotary kilns for final drying without need for crushing and sieving. The products were analyzed by infrared spectroscopy, which identified the product as pure sodium carbonate monohydate.

In laboratory experiments, New Sky produced soda ash using a non-evaporative "warm contact" process. Rather than supersaturating a solution of sodium carbonate by vaporizing water, this process generates supersaturated solution by reacting  $CO_2$  with very concentrated warm hydroxide (~40°C). As  $CO_2$  is absorbed, the concentration of sodium carbonate increases past its saturation point, and if the temperature is greater than 37°C, sodium carbonate monohydrate precipitates. To extend the process, solid hydroxide is added to maintain reagent concentrations. Benefits of this process include simplified equipment, lower capital costs, lower reagent costs and less energy consumption. The caveats include potential clogging of the contactor and the requirement for solid or highly concentrated hydroxide. Nonetheless, the process is unique to  $CO_2$  capture and mineralization strategies, may offer significant energy and GHG benefits, and warrants further study in Round II research.

#### Sodium bicarbonate

Sodium bicarbonate has an added carbon benefit compared to soda ash: it mineralizes twice the amount of CO<sub>2</sub> per mole of sodium hydroxide. Furthermore, processing does not require evaporation of large quantities of water and therefore has a much smaller energy demand for mineralization than soda ash. These advantages are counter-balanced with the requirement for relatively concentrated, pressurized carbon dioxide, which is a not readily available in flue gas. However such concentrated, pressurized CO<sub>2</sub> streams are widely encountered in sour natural gas streams, making bicarbonate production a logical low carbon product for New Sky to produce in Alberta.

New Sky was able to address the  $CO_2$  specifications required for bicarbonate production by working with Avery Brewing, which produces an ideal  $CO_2$  stream for bicarbonate production. The Avery gas stream did carry some aromatic chemicals from the brewing process, which were also captured by the hydroxide. However, a carbon filter upstream of the contactor removed any noticeable odor from the product. Analysis of the kinetics revealed that formation of bicarbonate is significantly slower (7-10 times) than formation of carbonate. Thus, optimizing mass transfer and  $CO_2$  input is important to drive the bicarbonate reaction. Despite forming solids in the contactor, the sparger did not clog and allowed the gas to flow uninhibited. Bicarbonate proved much easier to handle in a contactor than carbonate and is amendable to inline filtration. The post processing involves dewatering in a filter press and drying in stream of warm dry air. This resulted in a uniform, free-flowing product that required no further processing.

### Precipitated calcium carbonate

Precipitated calcium carbonate is a product that is used as a filler and whitening agent in many materials including paper, plastics and concrete. In many of the processing systems mention above, process water is generated with low levels of carbonate. It would be impractical to evaporate such large amounts of water to recover such a small amount of carbonate. Hence, New Sky demonstrated the precipitation of calcium carbonate as a final recovery of carbonate and a useful step in water management. The process involves addition of calcium chloride to a sodium carbonate solution, which immediately precipitates insoluble calcium carbonate. Post processing can be as simple as decanting the water to produce a concentrated slurry, or filtration followed by drying to make a uniform powder. The remaining sodium chloride solution can be recycled through the system several times before building concentrations require purging.

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# Processing Gas Streams with Variable CO<sub>2</sub> to H<sub>2</sub>S Ratios

Tara Yoder, PhD and Deane Little, PhD, New Sky Energy

### Introduction

During New Sky's Oklahoma pilot project we learned that very high  $CO_2$  to  $H_2S$  ratios (>20:1) in sour gas results in very low sodium sulfide concentrations in the resulting capture solution. This in turn minimizes the amount of sodium hydroxide recycling that can occur during multiple capture and regeneration cycles. Ideally, a balanced mix of  $H_2S$  and  $CO_2$  would maximize the GHG and energy benefits of New Sky's  $CO_2$  mineralization strategy.

To address this issue, in February 2016 New Sky R&D team began experiments to gain insight into the range of potential gas mixtures that can be efficiently treated using NaOH capture and SulfurCycle E electrochemistry. To that end, we utilized our sophisticated lab-scale scrubbers and SulfurCycle E reactor to test custom gas mixtures of H<sub>2</sub>S, CO<sub>2</sub>, and nitrogen. The goals of this study were to:

- 1. Observe the capture performance of NaOH solutions on gas mixtures,
- 2. Measure the electrochemical performance of these solutions and
- 3. Better understand the potential applications and markets for our technology.

# **Gas Scrubbing**

Customized gas mixtures containing various ratios of CO<sub>2</sub> to H<sub>2</sub>S were produced by mixing nitrogen, H<sub>2</sub>S, and CO<sub>2</sub> using mass flow controllers. Gas streams with CO<sub>2</sub> to H<sub>2</sub>S ratios of 1:1 (0.5:0.5 vol%), 5:1 (0.5:2.5 vol%) and 25:1 (0.1:2.5 vol%) were used to feed a bubble column containing sodium hydroxide solutions at flow rates of 3 SLPM (standard liters per minute). The gas streams were sparged through a 3-inch diameter, 4 feet tall PVC column with a rubber gasket sparger holding 1-2 L of 1-2 M NaOH capture solution.

The following graphs (figure 1) show the capture performance when the mixed gas stream contained equal amounts of  $H_2S$  and  $CO_2$  (1 vol% of each). On the left, the  $H_2S$  capture performance was > 99.9% for the entirety of the run until the solution was spent. On the right, the  $CO_2$  capture efficiency was observed to drop more rapidly than the  $H_2S$  capture efficiency, indicating a preference for  $H_2S$  capture when the NaOH solution was nearly spent.

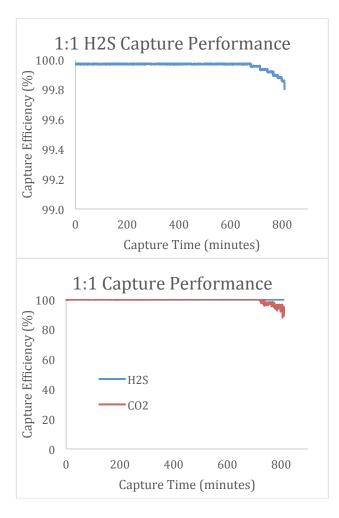
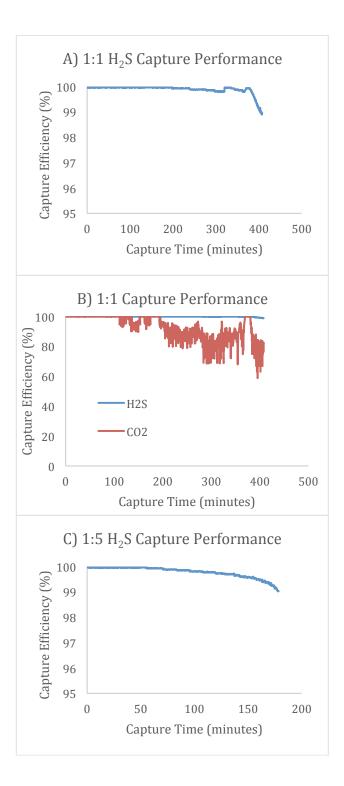


Figure 1: Capture performance for a 2 L solution containing 2 M NaOH. The gas stream contained 1 vol%  $H_2S$  and 1 vol%  $CO_2$ 

The graphs below (figure 2) display the capture performance when 1 L of 1 M NaOH was treated with gas streams containing  $H_2S:CO_2$  ratios of 1:1, 1:5, and 1:25. It was found that  $H_2S$  was somewhat preferentially captured over  $CO_2$  when  $CO_2$  was present in excess, with the mole ratios captured being 1:0.96, 1:3.86, and 1:16.86, respectively. This selectivity is important to our goal of removing  $H_2S$  from sour gas streams, as it is critical to reduce  $H_2S$  below 4ppm to produce pipeline quality gas.



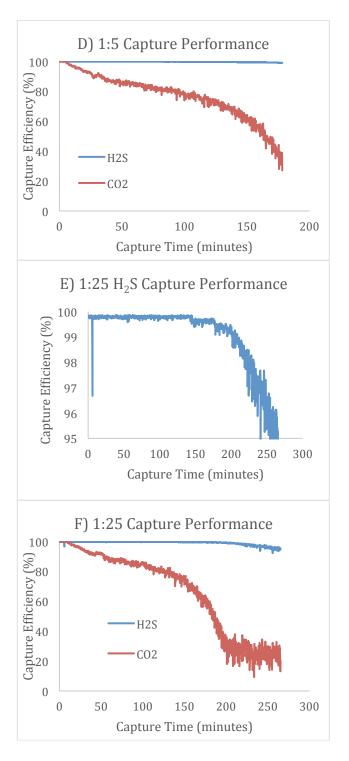


Figure 2: Capture performance for 1 L solutions containing 1 M NaOH.

The following table (figure 3) outlines the characteristics of the above scrubbing experiments. While the gas streams containing equal amounts of  $H_2S$  and  $CO_2$  were captured in relatively equal amounts, the caustic solutions selectively captured the  $H_2S$  when it was present in lower concentrations than the  $CO_2$ . Additionally, the amounts of

sulfide and carbonate captured totaled about half of the concentration of sodium, indicating the formation of sodium bisulfide and sodium carbonate according to the following equations:

$$H_2S + 2 NaOH \rightarrow Na_2S + 2H_2O$$
  
CO<sub>2</sub>+ 2NaOH → Na<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O

As the sodium is exhausted, the solution is able to capture some additional  $H_2S$  and  $CO_2$  based on the following equations:

$$Na_2CO_3 + H_2S \rightarrow NaHCO_3 + NaSH$$
  
 $Na_2CO_3 + CO_2 + NaHCO_3 \rightarrow 2NaHCO_3$ 

1.8416.91	Captare chart					
Figure No.	H <sub>2</sub> S:CO <sub>2</sub> Ratio Gas Stream	Volume % H₂S/CO₂	Molarity/Volume NaOH solution	H <sub>2</sub> S:CO <sub>2</sub> Ratio Captured	Na₂S Molarity	Na₂CO₃ Molarity
1	1:1	1/1	2.00 M/2 L	1:1.04	1.08 M	1.13 M
2 A-B	1:1	0.5/0.5	1.04 M/1 L	1:0.96	0.27 M	0.25 M
2 C-D	1:5	0.5/2.5	0.99 M/1 L	1:3.86	0.12 M	0.46 M
2 E-F	1:25	0.1/2.5	1.01 M/1 L	1:16.86	0.04 M	0.59 M

### Figure 3: Capture characteristics for caustic solutions

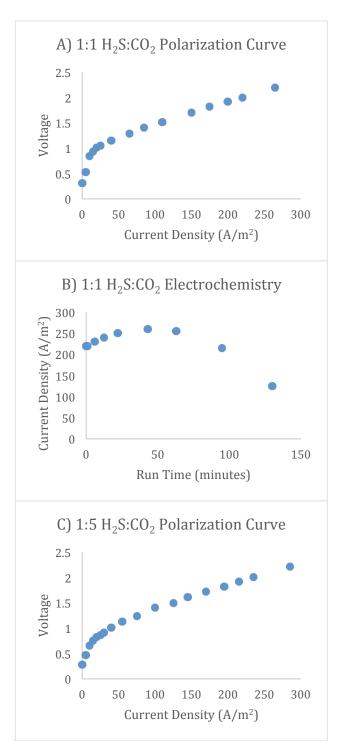
# Electrochemistry

Once the scrubbing step was complete, the resulting solutions were converted to sulfur and polysulfides using a SulfurCycle E electrochemical cell. The flow cell used the capture solutions as the anolyte with the following configuration: two chambers, graphite felt anodes and stainless steel cathodes with a surface area of 200 cm<sup>2</sup>, Nafion cation exchange membranes, and a 0.2 M NaOH catholyte.

Two experiments were performed on each capture solution. First, the applied voltage was swept from zero to 2.2 V (total cell voltage), while the current was recorded. Then the cell was run at 2V, monitoring the current achieved, until the current dropped significantly. The solutions from the experiments in Figure 2 were treated in this way and the results are displayed below in Figure 4 and 5.

As expected, the 1:1 ratio of sulfide:carbonate produced the best current densities, and the 1:25 ratio produced the worst. However, the surprising result was the 1:5 ratio: the solution gave current densities nearly as high as the 1:1 and reached a polysulfide chain length of nearly 4 compared to 3 for the 1:1 solution (see Figure 5). The 1:25 ratio only had a sulfide concentration of 0.04 M, resulting in a rapid drop off in current density during the experiment compared to the higher ratios. This decline may have been less

dramatic if a higher volume had been used to increase the total sulfide available for the electrochemical reaction.



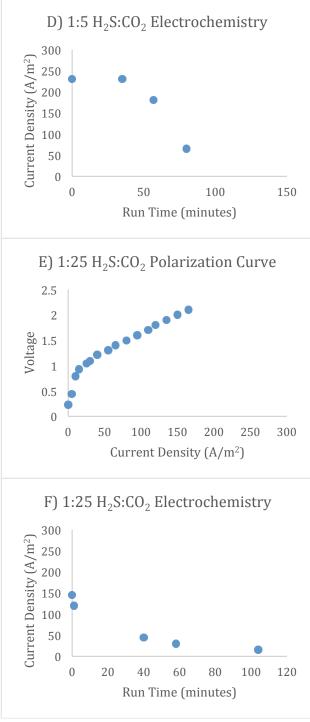


Figure 4

Figure No.	H <sub>2</sub> S:CO <sub>2</sub> Ratio Gas Stream	Volume % H <sub>2</sub> S/CO <sub>2</sub>	Na₂S Molarity	Na₂CO₃ Molarity	Max Current Density	Sulfide Chain Reached
3 A-B	1:1	0.5/0.5	0.27 M	0.25 M	260 A/cm <sup>2</sup>	3
3 C-D	1:5	0.5/2.5	0.12 M	0.46 M	230 A/cm <sup>2</sup>	3.9
3 E-F	1:25	0.1/2.5	0.04 M	0.59 M	145 A/cm <sup>2</sup>	2.5

#### Figure 5: Electrochemical characteristics for capture solutions

### Conclusions

Based on the results of this study, we concluded that operating the electrochemical cell on capture solutions from gas streams with less than a 10:1 ratio of  $CO_2$  to  $H_2S$  is recommended. At these ratios the sulfide ions contribute large amounts of energy to the cell, reducing the net energy cost and maximizing the GHG benefits of  $CO_2$ mineralization. Fortunately the great majority of sour gas fields in Alberta produce gas with  $CO_2$  to  $H_2S$  ratios in New Sky's preferred range. Similar concentration ratios could be achieved by other methods, such as precipitating the carbonate from a saturated solution, mixing the solution with more caustic, and capturing again. This process could be repeated cyclically until a sufficient amount of sulfide is present to perform electrochemistry. Most importantly, it was clear that a very broad range of  $CO_2$  to  $H_2S$ ratios (roughly 1:5 to 5:1) will allow effective SulfurCycle E electrochemistry and  $CO_2$ mineralization. These acid gas ratios are an ideal fit for Alberta, which holds trillions of cubic feet of sour gas with similar  $CO_2$  to  $H_2S$  ratios in reserve.

# CO<sub>2</sub> Capture and Mineralization at Avery Brewing

Megan Cousins and Joe Kosmoski, PhD

# Background

New Sky Energy's patented CarbonCycle technology (US Patent #8227127, also patented in Canada, China and Australia) captures  $CO_2$  from industrial exhaust streams such as flue gas, natural gas and fermenters converts it into soda ash, bicarbonate, and other useful carbonates. New Sky's CarbonCycle project with Avery Brewing treated brewery gas streams about to enter the atmosphere to capture  $CO_2$  from a relatively clean, concentrated source of gas. The resulting carbonate solutions served as excellent raw inputs for mineralization without all the challenges of pre-treatment required for flue gas operations. Applied to fermenter gas streams, CarbonCycle produces carbon neutral or even carbon negative carbonates. These mineralized  $CO_2$  products have many industrial uses, including glass manufacturing, plastics and construction materials.

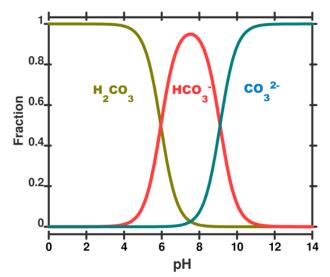
### **Chemical Principles**

Two CarbonCycle  $CO_2$  scrubbers have been installed at Avery Brewing to capture  $CO_2$  from their exhaust gases. A 2-liter scrubber provided quality control testing and  $CO_2$  analysis. This scrubber is attached to two  $CO_2$  sensors (one upstream and one downstream) for use in analyzing  $CO_2$  before and after capture in sodium hydroxide. A 200-liter scrubber column was used to produce concentrated sodium carbonate or sodium bicarbonate from sodium hydroxide solutions.

The chemical mechanisms taking place in this process are as follows:

1.  $2NaOH(aq) + CO_2(g) \rightarrow Na_2CO_3(aq) + H_2O(l)$   $k_1$ 2.  $Na_2CO_3(aq) + H_2O(l) + CO_2(g) \rightarrow 2NaHCO_3(s)$   $k_2 \cong 7k_1$ 

In practice, reaction 1 proceeds to completion before reaction 2 can occur. The production of carbonate is kinetically favored over the production of bicarbonate, indicated by the relative rate constants (*k* values) measured in the lab. It is also important to consider the state of matter of each reagent and product. Notably, bicarbonate can be directly produced as a solid precipitate without unit operations specific for mineralization, whereas carbonate requires crystallization to produce soda ash. The product endpoint for each reaction is determined from the pH. This is depicted in the following (figure 6):



*Figure 6: Speciation diagram for fraction of carbonate ions as a function of pH.* 

This graph reflects the fraction of carbonate ions that are present in solution as more and more  $CO_2$  is driven into solution (from right to left). When  $CO_2$  is absorbed into NaOH, Na<sub>2</sub>CO<sub>3</sub> is spontaneously formed and NaOH is consumed at pH range of 10-12. This is followed by kinetically slower formation of NaHCO<sub>3</sub> and consumption of Na<sub>2</sub>CO<sub>3</sub> at pH 8-10. Since formation of bicarbonate is a relatively slow reaction, cool concentrated  $CO_2$  is required to push the reaction to completion. Hence, Avery's exhaust is an ideal reagent for formation of bicarbonate, whereas most flue gas or natural gas streams are too dilute to drive the bicarbonate reaction to completion.

#### **Engineering Designs**

Over the course of the project at Avery Brewing, New Sky has greatly expanded its practical knowledge of scrubbing techniques and mechanisms. Below are some main points that were observed:

2-Liter Scrubber:

- The use of a bubble column for the 2-liter scrubber provided high liquid contact for incoming gas. This design was simple and tailored to the quality control aspect of the small scrubber.
- A carbon filter was installed upstream of the scrubber. Carbon filters have high surface area for adsorption and gas purification, especially when wet surfaces are available to help transfer the gas to the solid phase. The use of a carbon filter proved essential for removal of hops, oils, and other organics co-produced from the brewing process. It was also beneficial in odor control, as was observed by comparing products generated with and without the carbon filter.

200-Liter Scrubber:

- A 100-fold scale up of the scrubber had no observable effect on the function of the system.
- The large 200-liter scrubber was designed to accommodate several different operational modes including a traditional bubble column, falling film, and packed columns.
- The bubble column mode provided efficient and complete scrubbing of CO<sub>2</sub> due to the long residence time inherent to the design. However, brewery exhaust is close to atmospheric pressure and required a blower to drive the gas through the column. The blower was difficult to maintain for continuous operations in the challenging environment of the cellar floor, and consumed a relatively large quantity of energy. Thus, when minimizing the carbon footprint is a critical design consideration, the use of blowers is not recommended. Fortunately sour natural gas is generally pressurized, which allows highly effective, low energy bubble or packed column designs without need for a blower or pump.
- Packed column mode was not tested at Avery due to potential crystallization of minerals on the packing, and the requirement for a blower and circulation pump.
- Falling film mode was used for the 200-liter scrubber to create very high liquid turnover for long term CO<sub>2</sub> adsorption in a system that is not pressurized. This method proved effective and reliable at producing sodium carbonate and sodium bicarbonate with minimal energy requirements. Direct measurement of electrical draw from the system indicated that only 15% of the energy was required to run the falling film circulation pump compared to the bubble column blower. Any mass transfer advantages of the bubble column mode were negated by the high concentration of cool CO<sub>2</sub>, which allowed for high scrubbing efficiencies in falling film mode.

#### **Block Flow Diagram**

The following figure shows a basic block flow diagram of the movement of gas through the scrubbers installed at Avery Brewing:

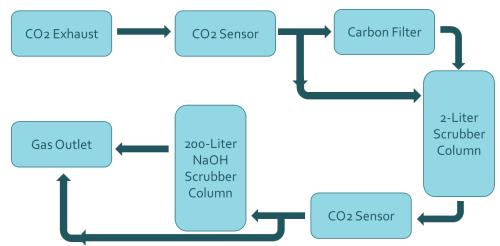


Figure 7: Block flow diagram for movement of gas flow through systems installed at Avery Brewing.

- Two scrubbers allow flexible operations. The gas can exit the system after the first scrubber, or can proceed to the 200-liter scrubber before exiting.
- The 2-liter scrubber can be used as a form of pre-treatment for the 200-liter scrubber.
- The carbon filter contains the option for bypass.

### **Process Flow Diagram**

The following figure shows a more detailed process flow diagram of gas moving through the 2-liter and 200-liter scrubbers installed at Avery Brewing. Initially, the 200-liter system was designed and deployed to study the mechanical aspects of different scrubber modes. Once the 200-liter system was ready to receive CO<sub>2</sub>, the 2-liter system was added to monitor gas flows, concentrations, and product quality.

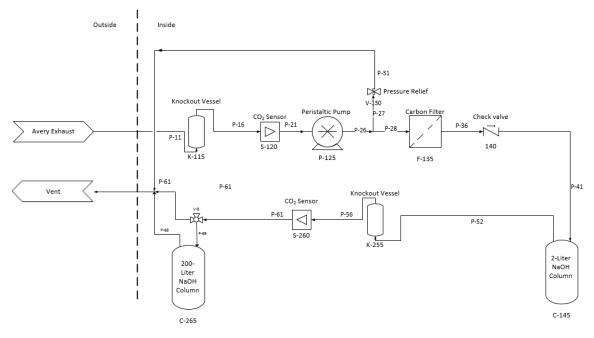


Figure 8: Process flow diagram for units installed at Avery Brewing.

- The 2-liter scrubber and associated process units are attached to a portable skid with built-in spill containment. Knock out vessels were incorporated into the design to prevent liquids from traveling through the system.
- A 3/8" stainless steel line taps directly into the CO<sub>2</sub> exhaust line, providing a slipstream of the exhaust gas.
- The 200-liter scrubber system was built as a standalone unit which could be tied into the 2-liter system as needed.

The following images show the 2-liter scrubber station and the larger 200-liter system as built. The two systems were installed on the brewery's cellar floor, which is a highly active area. Steam, foam, water, and temperature swings are common issues in brewery operations and were addressed by using industrially hardened equipment, design criteria, and compatible materials.



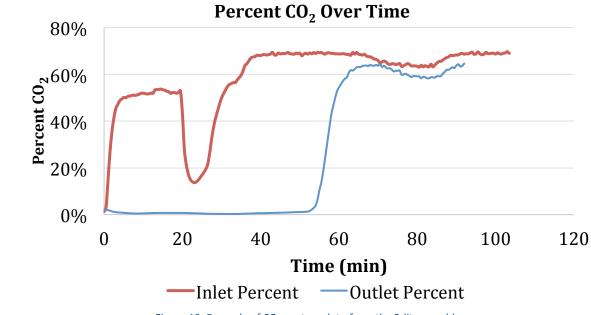


Figure 9: Images of the 2-liter system (left) and 200-liter system (right) at Avery Brewing.

#### Results

Below is an example of an experiment run in the 2-liter scrubber. The purpose of this experiment was to study the CO<sub>2</sub> patterns at Avery, as well as determine if the carbon filter removes organics carried in the exhaust stream before entering the scrubber.

- The maximum percent of CO<sub>2</sub> in the exhaust was measured around 69%. The exhaust was likely mixed with air before entering the CO<sub>2</sub> analyzer.
- There are fluctuations in the flow rate of CO<sub>2</sub> leaving the exhaust over the course of the day depending on which brewing process is underway.
- Two sources of CO<sub>2</sub> are generated at the brewery. The first originates from fermentation and the other is process gas used to blanket equipment.
- The sample shown scrubbed CO<sub>2</sub> through 1 liter of 2M NaOH. Note that essentially all of the CO<sub>2</sub> was removed from the gas stream over the course of an hour, after which time breakthrough occurred.



*Figure 10: Example of CO*<sub>2</sub> *capture data from the 2-liter scrubber.* 

### **Discussion and Moving Forward**

Installing scrubbers at Avery Brewing and running experiments with their CO<sub>2</sub> exhaust was beneficial in proving the fundamental ideas behind New Sky's CarbonCycle process, as well as understanding more about scrubbing mechanisms in large columns. Sodium carbonate that was produced in the large 200-liter scrubber was crystallized to make pure soda ash from this natural CO<sub>2</sub> source. The technology implemented at Avery Brewing forges a solid pathway to expanding the use of CarbonCycle globally.

An interesting route to further expand upon this technology could be a system that uses a three-phase reactor. CarbonCycle inherently and elegantly involves three phases of matter (gas, liquid and solids), and designing a system that can capture and mineralize  $CO_2$  in one cohesive unit is highly desirable. The falling film mode not only works well for absorbing gasses, but is amendable to in-line solids removal due to the constant flow of liquids. Literature on this topic is sparse, as most three-phase reactors pertain to a solid catalyst adsorbing the gas rather than a mineralization process happening within. Other literature pertains to direct mineralization of  $CO_2$  from flue gas (Werner et al.), which in itself is an interesting concept. All of these topics are viable for future directions of New Sky's CarbonCycle process.

# References

Werner M., Hariharan S., Mazzorri M. Flue gas CO<sub>2</sub> mineralization using thermally activated serpentine: from single- to double-step carbonation. *Phys. Chem. Chem. Phys.*, 2014, 16, 24978-24993.

# Greenhouse Gas Impacts

# Summary

The New Sky Process is a novel, very low energy method of sweetening sour gas that results in production of a number of valuable products. These include sweetened natural gas, carbonates made from captured CO<sub>2</sub>, and sulfur or sulfuric acid. The New Sky Process results in direct CO<sub>2</sub> emission reductions by:

- Capturing up to 6 MT/year CO<sub>2</sub> from sour natural gas in Alberta and converting it into useful carbonates such as soda ash and sodium bicarbonate
- Displacing "fossil carbonates" such as conventionally manufactured soda ash and sodium bicarbonate from the marketplace
- Dramatically reducing energy related CO<sub>2</sub> emissions in sour gas sweetening by replacing fossil fuel based thermal regeneration with energy efficient electrochemical regeneration of the capture solvent
- Regenerating sodium hydroxide, an important commodity chemical and reliable gas sweetening agent, with 75% energy savings relative to conventional chloralkali production
- Using co-product hydrogen in a fuel cell to further reduce the energy required to regenerate sodium hydroxide, resulting in up to 94% energy savings relative to conventional NaOH manufacturing, or if New Sky's technology displaced in the market, the production of hydrogen via electrolysis, it would displace the emission of 3MT/year CO2e

Quoting an April 2016 letter from Julie Sinistore, PhD, a GHG accounting expert originally hired by New Sky in 2013 to assess the carbon benefits of New Sky's process during our Round 1 CCEMC application:

"As a sustainability professional, my assessment of the New Sky Energy (NSE) process is that it is novel because it provides many opportunities for the reduction of the emission of Greenhouse Gases (GHGs) that contribute to Global Warming Potential (GWP). The NSE process is both energy efficient and produces multiple co-products. Two valuable co-products from the gas sweetening process are soda ash and sodium bicarbonate.

Finally, though not directly applicable in the conventional GHG emissions account methodology, it is important to note that producing soda ash and sodium bicarbonate from the carbon that would otherwise be released during conventional gas sweetening represents a re-use of that carbon and could potentially supplant the release of carbon from the production of these products from conventionally-mined ores. The combination of all aspects of NSE's multifunctional process makes a compelling argument for the substantial reductions in GHG emissions that could be realized from the full-scale implementation of their process.

# Direct CO<sub>2</sub> Benefits

In Alberta alone, New Sky's gas sweetening process has the potential to reduce direct  $CO_2$  emissions by up to 6 megatons per year. With 19% of Alberta's 2014 production of 4.6 tcf coming from sour gas, which contained as much as 10% CO2, we estimate that Alberta's sour gas contained over 7Mt of  $CO_2$ . For a sense of perspective, world reserves of sour gas containing >10 %  $CO_2$  are estimated at 700 tcf representing more than 36 gigatons of raw  $CO_2$  not counting combustion of methane from that gas. In Alberta, a portion of the acid gases from sweetening are re-injected, perhaps 0.5 - 1.0 Mt/yr of  $CO_2$ , slightly reducing the potential savings. By capturing the portion of  $CO_2$  in sour gas that is released into the atmosphere and using it to make carbonates for the North American market, New Sky's technology has the potential to reduce direct  $CO_2$  emissions in Alberta by as much as 6 Mt/yr. These benefits are focused entirely on the natural gas industry in Alberta; oil refinery operations may represent a comparable or larger opportunity to capture and convert  $CO_2$  and  $H_2S$  into useful chemicals.

New Sky proposes to incorporate this sequestered  $CO_2$  into soda ash and other carbonate/ bicarbonate products used in glass manufacturing, pulp and paper, agriculture, and other industries. Soda ash production in North America totals roughly 15 Mt/yr. By weight, this soda ash contains 6.2 Mt of  $CO_2$  that is later emitted when the soda ash is used in glass-making or other industrial processes. Coincidentally, the total direct  $CO_2$  emissions from gas sweetening processes are approximately equal to those from the North American soda ash industry. New Sky's process could displace these direct  $CO_2$  emissions, with  $CO_2$  that would otherwise be emitted in conventional gas sweetening processes, *effectively halving the combined direct carbon emissions of the sour gas and soda ash industries*. We are not including these savings in our calculations, but we do point out that New Sky's GHG reductions are sustainable both upstream and downstream and could accrue to either industry.

# Lifecycle Analysis Study

In order to examine the full lifecycle costs of the CO<sub>2</sub>-sequestering products, New Sky hired the LCA consulting firm PE-International. PE examined New Sky's mass and energy balance numbers and compared New Sky's lifecycle GHG emissions to established processes for soda ash and bicarbonate production. PE found that, relative to soda ash from trona, New Sky's process results in a 42 – 58 % reduction in cradle-to-gate (indirect) emissions and a 29 – 41 % reduction in lifecycle emissions (including release of CO<sub>2</sub> at the end of life, in the glass-making process for instance). By scaling these indirect emission reductions to the size of the soda ash market, we find that New Sky's process could reduce emissions by an additional 1.8 – 2.5 Mt/yr for a total GHG benefit of up to 8.7 million tons per year in North America. When compared to the Solvay Process

used overseas, PE found that New Sky's process results in a 63-73 % reduction in cradleto-gate emissions and a 49-57 % reduction in lifecycle emissions. If New Sky's process makes sodium bicarbonate, the GHG emission reductions are even greater.

# Hydrogen

One aspect that the PE assessment did not take into account is the added ability of the New Sky technology to produce hydrogen. When the additional co-production of commercial-grade hydrogen from New Sky's gas sweetening process is added to the other GHG benefits, a powerful picture emerges for the reduction of total GWP-causing gases. For every one kilogram of hydrogen produced by New Sky Energy's gas sweetening process, there is the potential to displace the production of hydrogen by conventional means such as cracking of crude oil or electrolysis. This displacement of hydrogen in the marketplace on a kilogram per kilogram basis has the potential to supplant the emissions of Greenhouse Gases (GHGs) from the production of hydrogen by conventional means. According to the Life Cycle Assessment (LCA) information available in the GaBi Database, the GWP of hydrogen produced via cracking and electrolysis are 3.18 and 51.8 kg CO2eq / kg hydrogen, respectively.

The relative weight of hydrogen to sulfur in H2S is 1:16. Approximately six percent of the weight of hydrogen sulfide that New Sky Energy treats will be converted to hydrogen gas that could displace the conventional means of production of hydrogen gas. Canada produces 6.8 Trillion Cubic Feet (TCF) of natural gas per year. Of this, 68% comes from Alberta and approximately 19% of this gas is sour. Of the sour gas, three and a third percent is H2S on average. This equates to the potential to produce 60,000 tonnes of hydrogen that could be produced via New Sky's technology per year. Using the conservative GWP for hydrogen produced via cracking (3.18 kg CO2eq / kg hydrogen), production of hydrogen with New Sky's technology could avoid the emission of 0.2 Mt of CO2e annually. If the hydrogen produced via New Sky's technology displaced the production of hydrogen via electrolysis (a best case scenario), then this would displace the emission of 3 Mt of CO2e annually.

# **GHG** Projections

Assuming an increasingly rapid adoption once the initial market proof has been established followed by a long tail of slower growth to capture the last fractions of market potential, New Sky projects 15Mt of CO2e in GHG benefits during the 1<sup>st</sup> 10 years following the project completion.

# GHG Reduction (Tonnes of CO2e):

Year/ GHG Value (Tonnes of CO2e) Year 1/ 20 Year 2/ 200 Year 3/ 10,000 Year 4/ 50,000 Year 5/ 250,000 Year 6/ 750,000 Year 7/ 2,000,000 Year 8/ 3,000,000 Year 9/ 4,000,000 Year 10/ 5,000,000

### Total 15,060,220 tonnes of CO2e

These calculations do not include the GHG benefits related to soda ash (or sodium bicarbonate) production, nor do they include the downstream benefits of lower cost production of natural gas from sour gas. Sour gas is expected to comprise a growing share of natural gas production in Alberta and around the globe. Lower natural gas pricing will facilitate faster transition away from high-GHG fossil fuels toward renewable sources which often rely upon natural gas to balance the power supply during periods of low winds or weather resulting in low PV values.

New Sky GHG emissions result from both electrical usage by SulfurCycle E and CarbonCycle reactors and heat consumption to produce dry crystalline carbonates. Using renewable electricity and waste heat minimizes these emissions and allows New Sky to produce  $CO_2$  negative carbonates.

# **Overall Conclusions**

1. As predicted in our 2014 CCEMC grant application, New Sky's SulfurCycle E gas sweetening process successfully converted large amounts of CO<sub>2</sub> in sour natural gas into useful carbonates, including soda ash and sodium bicarbonate.

2. Also as predicted, sodium sulfide formed by capture of  $H_2S$  was regenerated to form sodium hydroxide and sulfur/polysulfides at significantly lower voltages than expected for conventional sodium hydroxide production. These energy savings maximize the  $CO_2$ benefits achieved in Conclusion 1 above.

3. New Sky's patented CarbonCycle Process electrochemically converts sodium sulfate, an abundant natural resource in Alberta and Saskatchewan, into sodium hydroxide, sulfuric acid, hydrogen and oxygen. Unlike conventional sodium hydroxide synthesis, no chlorine by-product is formed, providing a sustainable pathway for CO<sub>2</sub> mineralization.

4. The four chemical products of the CarbonCycle process all have sustainable, low carbon synthetic uses. These include formation of  $CO_2$  negative carbonates (sodium hydroxide), digestion of cellulose into simple sugars for ethanol production (sulfuric acid) and combustion to produce zero carbon electricity or heat (hydrogen and oxygen).

5. New Sky scientists and engineers also developed a sustainable, cost effective gas sweetening process (SulfurCycle R), which selectively captures H<sub>2</sub>S from sour gas and converts it into elemental sulfur. SulfurCycle R media is a water-based metal oxide slurry, and can be regenerated simply by blowing air through spent media.

6. New Sky licensed its SulfurCycle technologies in the US to North Shore Energy. In 2016 New Sky successfully deployed SulfurCycle R at commercial scale (300K MCFD and 1M SCFD) at two sites in a North Shore owned sour gas field in SW Wyoming.

6. New Sky's suite of gas processing technologies can be deployed together or separately to treat the wide variety of gas streams that are usually present in sour gas fields in Alberta.

7. The great majority of sour gas wells in Alberta contain  $CO_2$  to  $H_2S$  ratios between 1:5 to 5:1, which overlaps the optimal range for SulfurCycle E operation.

8. Annually, sour gas produced in Alberta contains approximately 6 million tons of CO<sub>2</sub>, much of which is released to the air during gas sweetening or combustion. Use of SulfurCycle E, in combination with CarbonCycle and SulfurCycle R as needed, will allow Alberta oil and gas producers to cost effectively convert carbon dioxide in sour gas streams to carbonates, instead of releasing it to the atmosphere.

# Scientific Achievements

# Woodward Oklahoma Pilot Project:

- Successfully demonstrated SulfurCycle E capture of H<sub>2</sub>S and CO<sub>2</sub> from sour natural gas. Inlet gas stream flow was ~20 SCFM, H<sub>2</sub>S at ~300 PPM, CO<sub>2</sub> at 7000 PPM. Outlet gas was consistently less than 4PPM H<sub>2</sub>S (pipeline spec)
- Successfully demonstrated electrochemical conversion of sodium sulfide in spent caustic (NaOH) capture media back to sodium hydroxide. Process voltage and energy cost were significantly lower than conventional NaOH production, due to contribution of energy and electrons from captured sulfide
- Successfully converted captured CO<sub>2</sub> into ~50 Kg of dry carbonates, including soda ash and sodium bicarbonate
- Conceived, demonstrated, optimized and have now fully commercialized SulfurCycle R, a sustainable, water-based, onsite re-generable gas sweetening process. SulfurCycle R patents were filed in March 2016 and technology licensed in the US for O&G operations

# Avery Brewing Pilot Project:

- Designed, built and demonstrated 2 liter and 200 liter CarbonCycle absorber columns for CO<sub>2</sub> capture at Avery Brewing
- Demonstrated CO<sub>2</sub> capture and mineralization using a CarbonCycle absorber column at Avery Brewing in Boulder CO
- Produced high quality soda ash and bicarbonate from captured  $CO_2$  in a hot crystallizer

# Laboratory Results:

- Demonstrated that optimal CO<sub>2</sub> to H<sub>2</sub>S range for effective SulfurCycle E performance is 1:5 to 5:1. This range includes the great majority of sour gas wells in Alberta
- Optimized SulfurCycle electrolysis and determined ideal reactor design and construction
- Demonstrated effective methods of removing sulfides from carbonate solutions

# **Next Steps**

### Next steps / commercialization plans within two years of project completion.

New Sky has achieved promising technical and business validation of the company's SulfurCycle E, SulfurCycle R and CarbonCycle technologies in the US. This validation includes multiple successful pilot and now commercial scale projects (for SulfurCycle R), as well as multi-million dollar license agreements to a US based oil and gas industry partner. Commercial scale SulfurCycle R gas sweetening projects currently operate at a sour natural gas field in SW Wyoming, and a biogas sweetening pilot project has operated for the past 3 months at a Los Angeles wastewater treatment plant.

To achieve full success at New Sky's goal of commercial scale  $CO_2$  capture and mineralization, we need to build and operate a SulfurCycle / CarbonCycle demonstration plant in Alberta. Such a plant will allow New Sky to optimize and de-risk the technology and encourage Alberta oil and gas companies to invest in gas sweetening /  $CO_2$ mineralization plants based on New Sky's technology.

While New Sky's CO<sub>2</sub> mineralization / gas sweetening technologies has been proven to work in the field, New Sky needs to continue to expand its engineering and design expertise to address issues such as harsh winter weather and processing of concentrated acid gas streams, such as amine plant acid gas. Such enhancements to the technology can only come from projects with oil and gas partners, preferably in Alberta.

New Sky continues to work on acquiring additional partners from among Alberta's oil and gas companies. To date, New Sky has an LOI signed with Imaginea Energy for a commercial scale plant utilizing New Sky's SulfurCycle technologies to sweeten sour gas and mineralize captured CO<sub>2</sub> into valuable carbonates. To fund such Alberta-based energy projects, New Sky plans to apply for CCEMC Grand Challenge Round 2 funding.

If New Sky is successful in acquiring CCEMC Round 2 funding we will have the opportunity to demonstrate at commercial scale in Alberta that New Sky's gas sweetening technologies cost-effectively sweeten sour natural gas and produce commercially viable carbonates. At that point, New Sky would not require additional grant funds to deploy SulfurCycle and CarbonCycle commercially in Alberta. In the US, energy industry customers have already proven willing to finance New Sky projects, however these projects did not involve CO<sub>2</sub> capture and mineralization. In Alberta the price on carbon creates strong incentives for companies to reduce their CO<sub>2</sub> emissions. Additional customer or investor support would focus on accelerating the deployment of New Sky technology, and, given the advanced development of the technology and commercial proof in the US, such investment would offer rapid payback for customers.

New Sky has preliminary plans to open an office in Calgary, AB in 2017 to accelerate the commercialization of the company's technologies.

If New Sky is not awarded a Round 2 grant, we will focus on establishing proof in U.S. markets, where New Sky currently has sufficient funds and market traction for operations. Unfortunately US oil and gas companies are less interested in CO<sub>2</sub> capture and mineralization, but sour natural gas containing both H<sub>2</sub>S and CO<sub>2</sub> is very common and requires treatment. New Sky's SulfurCycle E, CarbonCycle and SulfurCycle R gas processing technologies provide multiple sustainable and cost effective strategies to treat such gas. Progress in the US marketplace may position New Sky to obtain strategic and investment partners in Alberta as well, but progress will occur much more quickly with Round 2 funding to support Alberta-based gas projects.

# Long-term plan for commercialization of the project technology/learnings.

New Sky plans to deploy its SulfurCycle and CarbonCycle technologies globally. Once operations in Alberta or the US demonstrate technical viability and market acceptance of our carbonate products, New Sky will work with oil and gas companies and glass manufacturers and other industrial users of carbonates to deploy New Sky technology around the globe.

New Sky is, or has already, secured worldwide patent protection for its technologies.

# Potential partnerships under development with technology integrators, adopters, etc.

In the US, New Sky works with North Shore Energy, sweetening sour gas under a longterm license of New Sky's technology. New Sky has also worked with the City of Boulder and LACSD (Los Angeles County Sanitation District) to pilot New Sky's SulfurCycle R technology to sweeten biogas produced during anaerobic digestion of sewage sludge. Upgrading biogas to renewal natural gas (RNG) is another potentially important application of New Sky's technology. Extending our partnerships into the mineralization of CO<sub>2</sub>, New Sky recently signed a letter of intent with Imaginea Energy to commercially deploy New Sky's sweetening and carbon mineralization technology in Alberta, which will be completed during Round 2 of the Grand Challenge Grant, if New Sky is selected.

New Sky has an existing business relationship with global glass manufacturer St. Gobain, related to use of New Sky soda ash produced from captured CO<sub>2</sub>. New Sky ran a successful feasibility study for St. Gobain, proving that St. Gobain could capture its own CO<sub>2</sub> to make soda ash needed for its glass manufacturing. New Sky has a standing order from St. Gobain for delivery of sufficient soda ash to supply an entire production run of glass (~100 tons of dry sodium carbonate). This is a scale achievable with commercial deployment of New Sky's SulfurCycle E and CarbonCycle technologies.

New Sky is also pursuing relationships with leading chemical and equipment suppliers to the oil and gas industry and with electrochemical reactor manufacturers. These relationships are intended to achieve sufficient scale for cost and reliability demanded by the oil and gas industry.

# **Communications Plan**

New Sky recently updated its website and completed a professional brochure describing its SulfurCycle and CarbonCycle technologies to prospective customers. New Sky uses these informational tools to engage prospective customers we meet at conferences and via introductions from interested parties.

New Sky regularly seeks speaking and exhibition opportunities at conferences in the US and Canada to present New Sky's innovative gas processing and CO<sub>2</sub> mineralization technologies.

In 2016, New Sky CEO Deane Little attended the following conferences:

Cleantech Forum, San Francisco, CA, January 2016 World Water Tech Investment Summit, London, UK, February 2016 Globe 2016 Sustainability Summit, Vancouver BC, March 2016 CO<sub>2</sub> Summit II, Technologies and Opportunities, Hyatt Tamaya, New Mexico, April 2016

At the Globe 2016 Sustainability Conference we identified an interested consultant who appears likely to order a SulfurCycle system for a Canadian wastewater industry client.

The same consultant has recently identified European companies that are interested in licensing New Sky's SulfurCycle technologies.

Dr. Little plans a trip to Alberta in June 2016 to meet with potential energy and wastewater industry clients as well as our CCEMC project manager Vicki Lightbown and other representatives from CCEMC and Alberta Innovates

Dr. Little will also attend the Calgary Stampede Investment Forum in July 2016