SkyMine® Carbon Mineralization Pilot Project

Final Phase 1 Topical Report

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Abstract: This Topical Report addresses accomplishments achieved during Phase 1 of the SkyMine® Carbon Mineralization Pilot Project. The primary objectives of this project are to design, construct, and operate a system to capture CO₂ from a slipstream of flue gas from a commercial coal-fired cement kiln, convert that CO₂ to products having commercial value (i.e., beneficial use), show the economic viability of the CO₂ capture and conversion process, and thereby advance the technology to a point of readiness for commercial scale demonstration and proliferation. The project will also substantiate market opportunities for the technology by sales of chemicals into existing markets, and identify opportunities to improve technology performance and reduce costs at commercial scale. The primary objectives of Phase 1 of the project were to elaborate proven SkyMine® process chemistry to commercial pilot-scale operation and complete the preliminary design (“Reference Plant Design”) for the pilot plant to be built and operated in Phase 2. Additionally, during Phase 1, information necessary to inform a DOE determination regarding NEPA requirements for the project was developed, and a comprehensive carbon lifecycle analysis was completed. These items were included in the formal application for funding under Phase 2. All Phase 1 objectives were successfully met on schedule and within budget.
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LIST OF ACRONYMS AND ABBREVIATIONS

AC = alternating current
CO₂ = carbon dioxide
CPM = critical path method
DC = direct current
DCAA = Defense Contract Auditing Agency
DOE = Department of Energy
EA = Environmental Assessment
EIV = environmental information volume
EPC = engineering, procurement, and construction
EVMS = earned value management system
FEED = front end engineering design
FEL = front end loaded engineering
GPM = gallons per minute
HAZOP = Hazard and Operability Study
HCl = hydrochloric acid
Hg = mercury
MSHA = Mine Safety & Health Administration
NEPA = National Environmental Policy Act
NETL = National Energy Technology Laboratory
NOₓ = nitrogen oxide
OSHA = Occupational Safety & Health Administration
P&ID = piping and instrumentation diagram
PFD = process flow diagram
PHA = Process Hazards Analysis
PMP = project management plan
ppb = parts per billion
PVC = polyvinyl chloride
RO = reverse osmosis
SO₂ = sulfur dioxide
Ton = short ton, unit of weight equal to 2000 pounds
Tonne = metric ton, unit of mass equal to 1000 kilograms
WBS = work breakdown structure
3PL = third-party logistics
1.0 EXECUTIVE SUMMARY

The SkyMine® Carbon Mineralization Pilot Project was awarded funding under USDOE/NETL Funding Opportunity Number DE-FOA-0000015, Technology Area #2 (Innovative concepts for beneficial CO2 use). Subsequently, Skonic Corporation and the Department of Energy executed a Cooperative Agreement for Skyonic to proceed with Phase 1 of a two-phase project to implement the SkyMine® technology, at a pilot scale, to capture 75,000 tonnes per year of CO₂ from a slipstream of exhaust gases from a cement plant kiln, and in so doing produce products with commercial value. The Project is to be conducted in two phases. Phase 1, which began on January 15, 2010, was originally scheduled to end on June 30, 2010, but was officially extended, by DOE issuance of a modification to the Cooperative Agreement, to September 30, 2010. Phase 1 consisted of executing the project tasks up to the point of establishing a final detailed design, conducting a NEPA review, and commencing construction. Additionally, recipients of Phase 1 funding had the opportunity to seek an extension of DOE financial assistance to enable work to continue under Phase 2 where the detailed design will be finalized, and the capture and conversion facility will be constructed and operated to show the readiness of the technology for commercial-scale demonstration. For this project, Skyonic Corporation assembled a competent project management team, augmented by subcontractors and other resources, to execute the approved project management plan (PMP) and deliver a detailed engineering and site-specific design and plant layout for a pilot SkyMine® facility. This Topical Report summarizes and details the activities performed and results realized from efforts in Phase 1 of this project.

Phase 1 activities included conceptual engineering, process characterization and testing, supply chain development, and preliminary design of the entire facility. To that effort, the extended project team worked with equipment manufacturers, host site entities, and regulatory agencies to produce a reference plant design, and a plan for building a pilot SkyMine® plant capable of capturing 75,000 tonnes (82,687 tons) of annually emitted waste CO₂ in Phase 2 of the project.

Engineering efforts included Aspen modeling and simulation, field tests, and laboratory work which enabled the team to both evaluate and validate the design concepts to be used for large-scale capture and mineralization of CO₂, and purification of products generated by the process. During Phase 1, the SkyMine® field test facility was moved and installed at the host site to further enable staff members to collect sufficient additional data and more fully characterize the emitted flue gas and various process conditions to allow model corroboration and process optimization for scale-up. Validation efforts were augmented by visits to a number of industrial plants operating equipment that is the same or similar to that being considered for the SkyMine® plant. Front end engineering design (FEED) studies were performed, and detailed bid packages and quotes were solicited from qualified vendors and evaluated by the team for performance, operating and capital costs, and sustainability.

Working with EPC firm Ford, Bacon & Davis, the team advanced the completion of process flow diagrams (PFDs), piping and instrumentation diagrams (P&IDs), material and energy balances, major equipment listings, and specifications and data sheets.

To best position the team for the Phase 2 (the Final Detailed Design, Construction, and Testing subphases), the Project Team managed Phase 1 to a work breakdown structure (WBS) two levels beyond reporting requirements and developed a detailed Phase 2 Project Management Plan. To
augment supply chain planning and help ensure a reliable and timely flow of raw materials to the plant, a detailed supply chain study was completed during this period.

In Phase 1, Skyonic completed a life-cycle analysis of the total carbon footprint benefit of capturing CO₂. This lifecycle model extends carbon-effect modeling to all inputs of the process (salt, water, electricity, transport). The complete analysis was submitted with the Phase 2 application.

The collaborative efforts of the Project Team and support entities have resulted in the design for a pilot SkyMine® plant capable of annual capture of 75,000 tonnes (82,687 tons) of emitted CO₂, and a detailed plan for building and operating the plant at the Capitol Aggregates’ Cement Plant in San Antonio, Texas in Phase 2 of the project. All of the necessary components, i.e. process flow diagrams, process verification, site and facility drawings, vendor and host site agreements, environmental permitting plans, and commercial off-take agreements, were addressed in Phase 1 to position the project to move forward with final design and construction in Phase 2.

Phase 1 of the project was managed within budget and to schedule with very limited variance. All Phase 1 project objectives have been accomplished and the project is fully prepared to move to Phase 2: construction and testing of the pilot facility.

2.0 Introduction

The Skyonic SkyMine® technology is designed to capture CO₂ from relatively dilute flue gas streams, such as those emitted by a coal-fired power plant or cement plant kiln, and convert the CO₂ into saleable carbonate or bicarbonate materials. Skyonic Corporation and the Department of Energy executed a Cooperative Agreement for Skyonic to proceed with Phase 1 of a two-phase project to implement the SkyMine® technology at a pilot scale in order to demonstrate the feasibility of operations at full scale. Phase 1 activities include process development and optimization for scale-up, conceptual engineering and testing, and preliminary design of the entire facility (to FEL 3 level engineering). These activities are prerequisites to the commencement of construction of the pilot facility. Phase 1 grant recipients were invited to submit Renewal Applications during Phase 1 in order to receive continued DOE support for Phase 2. This Topical Report describes activities conducted during Phase 1, and the results of those activities.

The primary objectives for Phase 1 were to use a SkyMine® field test facility to elaborate the known SkyMine® process chemistry to pilot-scale operation; to design a reference plant design to be built and operated in Phase 2, including specification of all input and output physical variables; to make refinements in cost and efficiency of the design of sub-processes and their integration into the overall pilot project system to be built in Phase 2; to augment the empirical data with process simulation in order to gain insight into the critical operating parameters; to develop engineering documents to a recognized standard level of detail that supports an appropriation-grade, site-specific estimate; to apply these basic design data in developing all information necessary for meeting NEPA and state and local environmental permitting requirements; and to further develop the Project Management Plan (PMP) for Phase 2 to Level 4/5 WBS that reflects the knowledge gained during Phase 1. Additionally, Task numbers 7.0 (Construction) and 8.0 (Testing) were added to the PMP for Phase 2 activities. Secondary objectives included exercising the Project Management Plan to keep Phase 1
work on schedule and within budget and best position the project team to successfully execute Phase 2 of the project.

3.0 EXPERIMENTAL METHODS (PROCESS DESIGN, R&D, SITE PLAN)

With the overall objective of designing and building a SkyMine® pilot decarbonation plant, Skyonic Corporation assembled a competent project team to produce a detailed process engineering and site-specific design and plant layout for a pilot SkyMine® plant in San Antonio, Texas. Close engagement with Skyonic-retained EPC firm, Ford, Bacon & Davis from the conceptual stage and through Phase 1 of this project focused on designing an optimal SkyMine® plant. The Project Team, to include FB&D, has engaged with numerous additional organizations, including various subcontractors and equipment manufacturers, host site entities, and regulatory agencies to produce a reference design, and a plan for building a pilot SkyMine® plant capable of capturing 75,000 tonnes (82,687 tons) of annually emitted waste CO₂ in Phase 2 of the project.

To further this effort, Skyonic Corporation collaborated with state-of-the-art manufacturers of key equipment, as well as best-in-field integrators to establish a design and build plan that achieves the project objectives.

Preliminary and early detailed design was facilitated through regular engineering meetings and measured deliverables, sophisticated process modeling and simulation, and internal and independent laboratory work. Site planning was facilitated by multiple site visits and planning meetings, detailed drawings, aerial and terrestrial photographs, historical research, and topographical analysis.

Secondary, yet important design criteria include efforts to minimize waste effluents, and incorporate state-of-the-art filtration and recirculation systems to shrink water usage to the lowest achievable levels.

3.1 PROCESS DESIGN

The SkyMine® Process is a unique, patented process designed to remove carbon dioxide from a gaseous waste stream, convert the carbon dioxide to a mineralized carbon product, and produce valuable chemical byproducts. The SkyMine® process, which reacts carbon dioxide from waste flue gas with sodium hydroxide to form sodium bicarbonate, is designed as a multi-column system. In the on-site field test unit, columns are equipped with recirculation pumps, metering pumps, pH sensors, temperature sensors, pressure sensors, sample points (for fluid samples), test points (for gas samples), drip trays (for fluid distribution), flow indicators and manual valves to control recirculation flow. The SkyMine® process is designed to remove over 90 percent of the carbon dioxide from a flue gas stream. The resulting products produced by the process are of high purity, and readily marketable.

The process of dewatering is dynamic and involves many variables. The test methodology involved isolating as many of these variables (e.g. materials selection, flow rates) as possible to determine the optimum for each case relative to design objectives.
Project engineers also worked with multiple vendors to characterize the dewatering and drying processes and determine optimum operating conditions to minimize energy consumption and produce a consistent marketable product.

The SkyMine® process is described below, in detail, by each of the nine process “areas”, identified as Areas 100 - 900:

Area 100 – Flue Gas Preparation and Processing

General

Flue gas from the cement kiln is the carbon dioxide source for sodium bicarbonate to be produced by the SkyMine® facility. The purpose of the flue gas preparation area is to acquire the required amount of flue gas from the kiln, and bring it to the required pressure and temperature for use in downstream processing. Cooling the flue gas to the required 104°F (40°C) is accomplished through a fin tube heat exchanger. Condensate from the cooling operation is removed from the gas stream and further processed for either use in the process or in preparation for removal from the site as waste. Major equipment in the flue gas preparation area consists of the following equipment:

- Flue Gas Blower
- Flue Gas Cooler
- Knock Out Tank with an associated demister and pump
- Condensate Pump
- Carbon Filters (2)
- Process Waste Tank and Pump

Flue Gas Analysis and Transport

Flue gas is transported from the flue gas stack to the blower in 48” FRP circular duct work. Prior to the blower the flue gas will be analyzed for total flow, opacity and gas stream content of CO₃, CO₂, SOₓ, and NOₓ. The opacity meter will provide a means of indicating problems with the Capitol Aggregate bag filters. A signal from the opacity meter will be transmitted to the SkyMine® control room to allow the blower to be stopped if there is a bag rupture in the bag house. An automated knife gate valve may also be closed if flue gas flow from the stack needs to be halted for any reason.

It is important to be able to quantify the carbon removed from the flue gas. To accomplish this, measurements will be taken at several locations in the process. Initial analysis of the gas entering the SkyMine® process will occur upstream of the flue gas blower. An annubar type flow meter will be used to measure the total flow of the flue gas. Flue gas composition will be recorded with an emission analyzer device.

The Flue Gas Blower is sized to move 22,000 acfm of flue gas, an amount calculated to deliver the required carbon dioxide to the process. The blower will be equipped with an inlet fan to protect against any particulates present downstream of the Capitol Aggregate bag
filters. The blower will also be equipped with a variable speed drive. The speed of the blower will be automatically adjusted based on a pressure reading in the knock-out tank downstream of the blower to insure flue gas is available to both the CO₂ Absorber Columns and the Bubble Columns. The variable speed drive may also be adjusted in the SkyMine® control room if the flue gas flow needs to be varied as the facility is started up or shut down.

**Flue Gas Heat Exchanger**

The Flue Gas Cooler is designed to cool the flue gas from its initial temperature of 264°F down to 104°F. Raw flue gas contains condensable compounds that will drop out of the gas stream as the stream is cooled. This condensate will be predominantly water but will also contain SOₓ, NOₓ, Hg, Pb, and other impurities. Gas flow will be directed vertically downward through the heat exchanger before exiting at either a 90 or 180 degree angle allowing condensate to be collected at the bottom of the heat exchanger and removed for further processing. All flue gas contacting surfaces of the heat exchanger will be covered with a specified coating, or an equivalent, to protect against the corrosive nature of the flue gas condensate.

Heat is removed from the flue gas by passing it over a series of fin and tube exchange banks. The banks are divided into three cooling regions each with a different cooling media. Flue gas first contacts cooling water in a pressurized loop. Heat is transferred from the flue gas at its highest temperature to Loop Water where it is used to heat gasses entering the bicarbonate dryer. The flow rate of the loop water will be manually set at approximately 54 gpm at a pressure of approximately 62 psig. Loop water is expected to enter the heat exchanger at approximately 145°F and exit at 219°F. At 62 psig, the water will still be in the liquid phase. This allows for harvest of high quality heat from the flue gas using a gas to liquid heat exchanger, which has better heat transfer than a gas to gas exchanger. The flue gas was modeled to exit Region 1 of the heat exchanger at 170°F.

The second cooling region utilizes cooling tower water to cool the flue gas from approximately 170°F to 120°F. It is during this region of cooling that precipitation from the flue gas is expected to begin. Much of the latent heat of condensation is removed in this region. Cooling tower water flow is manually set in Region 2 at approximately 520 gpm producing a temperature rise from 85 to 105°F.

Coolant flow in Regions 1 and 2 is accomplished by adjustment of the manual valves on the outlet of the coolant lines. Temperature indicating gauges are provided on both sides of the heat exchanger to aid in finding the correct settings.

In Region 3 of the Flue Gas Heat Exchanger, cooling is accomplished with chilled water. Here the flow of chilled water is designed to be automatically controlled to produce a flue gas outlet temperature of 104°F. Chilled water flow is expected to be approximately 417 gpm for a 10°F temperature rise from 45 to 55°F in the chilled water. Flue gas temperature is expected to drop from 120 to 104°F in this region. Additional material is condensed from the flue gas stream.
Because the quantity and impact of particulate in the flue gas is unknown, provisions are made to clean the fins. Sight glasses and light ports will be provided to allow observation of any solids build-up. Ports will be provided to spray water onto the fins to remove build-up and debris. At present, this is designed to be a manual operation.

**Flue Gas Knock-Out Tank Operations**

The Flue Gas Knock-Out tank serves to remove any remaining condensate from the flue gas stream prior to its transport to the columns. It also serves as a collection point for condensate from the flue gas heat exchanger before the flue gas compressor.

Cooled flue gas exiting the heat exchanger travels via a 36" round FRP duct. To aid in further removal of SO\textsubscript{x} and NO\textsubscript{x} from the flue gas, the gas stream is passed through a dilute caustic spray upstream of the knock-out tank. The caustic reacts with remaining SO\textsubscript{x} and NO\textsubscript{x} and is removed from the gas stream as reacted condensate. The quantity of caustic is controlled to produce a pH set point in the exiting condensate from the knock-out tank. The set point can be adjusted during operation to produce balance between optimal absorptive characteristics for passage of the stream through the carbon filters and minimal loss of CO\textsubscript{2} to the condensate stream. The water flow rate is adjusted manually with the aid of a rotameter to dilute the 20% caustic stream to a concentration of approximately 2%. The concentration does not need to be exact.

The gas stream from the knock-out tank exits through a demister before traveling to either of two CO\textsubscript{2} absorber columns or either of two coolers associated with the reaction columns.

Condensate from the flue gas heat exchanger flows to the flue gas knock-out tank via a 3" gravity drain line. Condensate streams from the operations around the reaction column portion of the plant are collectively pumped via a condensate pump to the flue gas knock-out tank. Condensate collected from the bottom of the knock-out tank is pumped to a carbon filter. The knock-out pump is sized for the expected combined condensate flow of 16 gpm. Liquid level in the knock-out tank is maintained using a level control valve downstream of the pump. A high level switch provides a means of alarming on high liquid level.

Pressure within the knock-out tank is measured and transmitted to the blower to control the blower speed. This control is described with the blower.

**Flue Gas Condensate Carbon Filters**

Carbon Filters are used to adsorb mercury, lead, and other impurities from the flue gas condensate. Each filter bed is sized for up to 25 gpm. Diverter valves are used to allow flow through the carbon beds in series or through either bed individually. Normally, the condensate stream will flow through the beds in series. A sample port located between the beds will allow monitoring for breakthrough of contaminants from the first bed. When this occurs flow will be diverted to pass through the second bed only and the first bed will be repacked with fresh activated carbon. Following repacking, the beds will be placed in series once again with bed two now serving as the lead carbon bed. Spent carbon will be disposed as waste and the vessel repacked with fresh carbon.
Pressure indicators are located on both sides of the carbon filter to allow a visual check of pressure drop across the beds.

**Column Vent Condensate**

Flue gas exiting the top of the carbonate and the bubble columns will be returned to the Capitol Aggregate flue stack. As the vented gasses cool, condensation will occur. The condensate will be collected and pumped via an air driven condensate pump to the Process Waste Tank described below. It is anticipated that about 10 gpm of condensate will be produced and sent to process waste.

**Process Waste Tank**

The process waste tank provides a place for collecting relatively clean water from this area of the SkyMine® facility. Filtered condensate flows at approximately 16 gpm from the carbon filter beds to a process waste tank. Column vent condensate is expected to produce approximately 10 gpm of waste flow. The tank also collects waste from the membrane filter return. Flow from the membrane filter return is intermittent, occurring five times per day for a total of 1,250 gallons per day. The tank provides slightly less than two hours of hold time for waste.

By the time the waste gets to the process waste tank it should be in excess of 99% water. If, after the beginning of operation it is determined that no hazardous impurities are present in the water, it may be possible to recycle the water back into the process. Spare nozzles are provided on the tank to allow for pH adjustment. A pH probe and transmitter are provided on the tank in addition to a sample port.

Until the purity of the water can be verified in operation, waste from the tank is pumped to a plant waste water tank. The pump is sized for the expected flow of 30 gpm. Liquid level in the knock-out tank is maintained using a level control valve downstream of the pump. An overflow line provides protection against high levels in the tank. A simple external level gauge is provided on the side of the tank to allow quick determination of the quantity of waste in the tank.

**Area 200 - CO₂ Absorption Columns**

**General**

Once the flue gas has been cooled to 104°F in the Flue Gas Preparation Area, 43% of the total flue gas is passed through a pair of CO₂ Absorber Columns operating in parallel. The columns provide a large vapor liquid contact area between flue gas flowing upward through the column and 20% NaOH solution flowing downward. Here the CO₂ in the flue gas reacts in the following reaction to form sodium carbonate:

\[
\text{CO}_2 (g) + 2 \text{NaOH (l)} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}
\]

The sodium carbonate solution is then fed to the bubble columns where it is further reacted with flue gas to yield sodium bicarbonate (NaHCO₃).
Major equipment in the CO$_2$ Absorber Column Area consists of the following equipment:

- CO$_2$ Absorber Columns (2)
- CO$_2$ Absorber Pump (2)

Each of these items is discussed in greater detail below.

**CO$_2$ Absorber Columns**

The CO$_2$ absorber columns, constructed of 304 SS, are 6 ft in diameter and 50 ft tall. Each column contains two approximately 15 ft sections of packing. Flue gas, cooled to 104°F, is introduced at the bottom of the column and flows upward to the lower bed. Caustic, produced via the chlor-alkali process, is diluted to 20% concentration and fed to the top of the column through a distributor and flows by gravity downward through the column.

The carbon dioxide in the flue gas feed reacts rapidly with caustic to produce sodium carbonate and water. More than 99% of the CO$_2$ from the flue gas reacts to form sodium carbonate and is removed from the gas stream and pumped from the bottom of the column with water. After passing through a demister to remove any entrained liquid, any unreacted CO$_2$ passes from the column with the stripped flue gas.

Manways are provided at the top and bottom of the column and at locations above and below each packed section. Manways located in the packed sections will be curved to the contour of the column wall to prevent disruption of flow in the packing.

Monitors are provided at the column exhaust to collect data on the quantity and composition of the stripped gas. Temperature and pH are monitored at the base of each packed sections as well as for the column bottoms. Sample ports are available at the base of each packed section to allow further analysis. The liquid level in the bottom of the column will be monitored and controlled using a level control valve downstream of the absorber pump.

**CO$_2$ Absorber Pump**

Prior to being fed to the bubble column, the sodium carbonate – water mixture is pumped from the bottom of the absorber column to a hold tank where it is mixed with the carbonate concentrate stream from the membrane filters. The pump is sized at 77 gpm to remove the liquid at the rate it is produced in the absorber column. There is one pump for each absorber column.

**Area 300 – Bicarbonate Crystallization, Separation, and Water Recovery**

**General:**

The major processes in Area 300 are sodium bicarbonate crystallization, separation, concentration and water recovery. Bicarbonate crystallization is the continuous process by which conditioned flue gas is compressed and bubbled through a saturated sodium carbonate solution in a bubble column reactor to precipitate bicarbonate crystals. The slurry is separated by a centrifuge into solids, sent to the dryer, and liquids, which are further
processed by high pressure membrane filtration. The membrane filter system concentrates the remaining carbonate and bicarbonate in solution while recovering water for reuse in the plant. The concentrated solution is recycled to the bubble column reactor for further reaction to allow zero product waste.

Area 300 includes the following major equipment:

- Compressors
- Flue gas coolers
- Sodium Carbonate cooler
- Knockout pots
- Bubble column reactors
- Decanters
- Membrane Filter package

**Flue Gas Compression:**

Conditioned flue gas from Area 100 is blown to each flue gas compressor package via FRP duct at a rate of 4,145 acfm with conditions of 30 inches of H₂O and 104°F (40°C). Flue gas is compressed using a rotary screw compressor to 38 psia and is cooled to 120°F (50°C) by the compressor package cooler using cooling water. The flue gas must be further cooled to 77°F (25°C) and the condensate removed before entering the bubble column reactor. This is accomplished using a chilled water after-cooler followed by an FRP knockout pot. The flue gas condensate is gravity drained from the after-cooler to the local knockout pot, then pumped to the main flue gas knockout tank using an air driven condensate pump. The flue gas enters each bubble column at 77°F (25°C) and 37 psia. This occurs in two identical trains and feeds 1,565 acfm of compressed flue gas to each respective bubble column reactor.

**Bubble Column Reactor:**

Downstream of the sodium carbonate scrubber column, the saturated carbonate stream is pumped to the carbonate column collection tank. Here it mixes with the membrane filter concentrate stream which is very similar in composition and pH. The mixed carbonate stream is cooled to 104°F (40°C) before reacting with 77°F (25°C) flue gas in the bubble column. The bubble column reactor dimensions are 70’ tall and 16’ diameter. The bubble column design includes a liquid distributor for the inlet sodium carbonate stream and trays in the upper section. Precipitation occurs in the core of the column as the newly formed slurry is recirculated via external downcomers. In the bottom section, the flue gas inlet sparger is located above the downcomer return and slurry is removed from the column base.
In the upper section of the column, a demister removes suspended liquids before the flue gas exhaust leaves the column at 3000 acfm. Just below the demister, the saturated carbonate solution enters the column through a liquid distributor at a flow rate of 145 gpm. The liquid distributor and tray section is separated by the liquid level, which is maintained by a level controller. The trayed section is used to prevent liquid backmixing.

The middle section contains the core of the column, where the majority of mass transfer and crystallization occurs. The flue gas bubbles create a buoyant force which drives liquid up the column core. Liquid recirculation tubes transfer liquid downward from the base of the trayed...
section to a tangential return near the flue gas inlet. This fluid motion also allows laminar flow up the column core which inhibits bubble coalescing.

Compressed flue gas enters the bottom section of the bubble column reactor through a sparger to create an optimal bubble size. Smaller bubbles allow quicker and more efficient mass transfer of CO$_2$ to the liquid phase to convert carbonate to bicarbonate. This reaction exploits the difference between the high saturation point for sodium carbonate and the lower saturation point for sodium bicarbonate. When this reaction occurs, the saturated stream of sodium carbonate reacts with CO$_2$ to form sodium bicarbonate. All bicarbonate formed above the saturation point precipitates and is removed as slurry for further processing at a rate of 150 gpm per bubble column. By precipitating only sodium bicarbonate crystals, the bubble column reaction ensures a high purity bicarbonate product that is suitable for food grade.

**Solids Separation**

The slurry recovered from the bubble column reactors is collected in the decanter feed tank which acts as a buffer between the bubble column and decanters. The slurry is agitated to keep the solids suspended and also provides a consistent mixture to the decanters. Two steep scroll decanters operate in parallel to separate the bicarbonate crystals to less than 10% moisture. The wet bicarbonate crystals are gravity fed into the dryer feed hopper at a rate of 6 cuft/min. The centrate is collected in the centrate tank and pumped into one of two membrane filter batch tanks at a flow rate of 265 gpm.

**Concentration and Water Recovery**

The concentrate is a saturated solution of sodium carbonate and bicarbonate. Using a reverse osmosis membrane filtration system, the centrate can be separated into water and a concentrated solution of carbonate and bicarbonate. The technology chosen by Skyonic to concentrate this solution is membrane filter. This system uses high frequency vibrations to shear the surface of the membrane to prolong the onset of filter plugging from solids. The membrane filter system allows the solution to be concentrated beyond the saturation point and precipitate during filtration. The optimum operation point for Skyonic is to recover 50% of the water per batch, which is just beyond the saturation point. The membrane filter system contains two batch tanks which are alternated to allow the overall process to remain continuous. In each batch operation, the centrate is pressurized via multistage progressive cavity pumps to overcome the osmotic pressure of the solution. The high pressure centrate enters the membrane filter pots where some water permeates the membrane per pass while the carbonate and bicarbonate are recirculated to the batch tank. The batch is complete when 50% of the water permeates the membrane and the liquid level inside the batch tank reaches the low level position. The concentrated carbonate solution is pumped out of the batch tank to each bubble column feed tank to mix with the carbonate stream as described above. This maintains the condition that 100% of the caustic entering the system exits as bicarbonate product. The water permeate is recovered from membrane filter and collected in the membrane filter permeate tank. 100% of the water is recycled for caustic dilution, brining, and cooling tower make-up. The membrane filter system is the key to allowing zero waste of product or water.
Area 400 – Sodium Bicarbonate Drying and Rail Loadout

General

After sodium bicarbonate is produced in the bubble columns and has been dewatered it must be dried and stored for shipment.

The sodium bicarbonate drying and rail loadout system includes the following equipment:
- Dryer Air Blower
- Dryer Air Heater
- Cooling Loop Pump
- Expansion Tank
- Bicarbonate Dryer Package
- Bicarbonate Conveying Package
- Bicarbonate Storage Silo 1 & 2
- Bicarbonate Loadout Package

Dryer Air Heating

Ambient air is heated from 89°F (32°C) to 162°F (72°C) by an air to a liquid heat exchanger. Air is conveyed by a Dryer Air Blower at a rate of 14,000 ACFM at 10 inches H₂O. An inlet air filter is used on the suction side of the dryer to prevent dust from entering the system.

The heating medium is a closed loop water system. Water is pumped at a constant 50 GPM to two heat exchangers in series. Cooling water leaves the flue gas cooler at 213°F. The heated water is then used to heat dryer air at a rate of 14,000 ACFM. The cooling water exits Dryer Air Heater at 145°F and returns to the inlet of the flue gas cooler. A back pressure valve is used on the outlet line of the liquid heat exchanger to ensure a pressure of 12 psig or greater is achieved in the cooling loop. An expansion tank allows for thermal expansion of water in the cooling loop.

Sodium Bicarbonate Drying

Sodium bicarbonate containing 10 wt% moisture is gravity fed from two decanters to the Bicarbonate Dryer Package at a rate of 6 cuft/min. Sodium bicarbonate is introduced to the drying chamber using a live bottom quad screw feeder. The dryer is 54 inches in diameter and 18 feet long. A natural gas burner system provides the additional heating necessary to provide complete drying within the dryer package. Heated air from the dryer heater enters a natural gas burner at 162°F (72°C) and exits the burner at approximately 600°F (316°C). The natural gas burner system includes an IRI or FM approved package fuel train with a flame supervision system, high limit controller and temperature controller. The heated air and product flows concurrently through the drying chamber into a reverse jet bag house. Dried sodium bicarbonate collects at the bottom of the bag house. The product will be dried to less
than 1% moisture to ensure flowability. A rotary airlock discharges dried sodium bicarbonate at a rate of 40,000 lb/hr to the sodium bicarbonate conveying package.

**Bicarbonate Conveying, Storage, and Loadout**

Dried sodium bicarbonate is conveyed by a dense phase pneumatic conveying system. Air is compressed in a small tank and released to transfer slugs of product to the silos. Dried sodium bicarbonate can be conveyed to one of two silos. A diverter valve is used to choose the final destination of the sodium bicarbonate. The silos are sized to hold approximately 12 hours of sodium bicarbonate production, each. The silos have a 14’ diameter with a 60’ height and 60 degree cone bottom with a total capacity of 7,328 ft$^3$. During filling operations, a bin vent provides sufficient breathing to allow displaced air to escape the silo while capturing any entrained dust.

The bicarbonate silos are located beside the dryer. A second conveying package transfers the product 800 feet to the rail loadout station. This package is also a dense phase pneumatic system. A dustless loadout spout, capable of 6 feet of vertical travel, will be used. A dust sock will be manually attached to the other railcar manway to capture any dust from the rail car during loadout.

**Area 500 – Salt Unloading and Brine Saturation**

**General**

Equipment Associated with Salt Unloading and Brine Saturation include the following:

- An Enclosed Salt Unloading Building with Dust Collector
- A Salt Receiving Hopper with a dual screw conveying system
- A Tubular Drag Chain Conveying System
- A Salt Storage Silo
- Brine Saturation System with 3 Salt and associated Brine Pits
- Brine Feed Pumps

Each of the items is described in greater detail below.

**Enclosed Salt Unloading Building with Dust Collector**

Salt will be transported to the site in hopper bottom semi trucks. The Unloading Building will be built over the receiving hopper and will provide a place for the salt to be unloaded while minimizing cross-contamination between the feed salt and the surrounding chemical and cement facilities. The building is designed for trucks to enter at one end of the building and exit the other. Automated roll up doors will close on either end of the building to enclose the operation. During operation, the entrance door of the unloading building will open and the truck will drive into the building and position the bottom hopper over the receiving pit. The truck will discharge salt from the hopper into the receiving tank. After the salt has been dumped the roll-up door on the exit side of the building will open, allowing the truck to leave.
The trucks will hold a nominal 45,000 lbs of salt. The salt being unloaded is coarse, typically 1/4"-1/2" though fines will be present. Clumping is also possible in the raw feed salt. At full production it is estimated that 17.5 trucks will be unloaded per day.

A dust collector with an integral blower will be supplied to collect salt dust from the salt unloading operation. The same dust collector will be used to collect dust from the storage silo discussed below. The dust collector will be located on top of the unloading building above the unloading pit. Salt from the dust collector will be periodically dumped into the receiving pit below via a rotary valve at the base of the collector.

**Salt Receiving Hopper with Dual Screw Conveying System**

A Salt Receiving Hopper is located within the Salt Unloading Building and provides a place for the salt-containing semi-trailers to discharge their load. The receiving hopper is sized at 12 ft long by 6.5 wide at the opening and 10 ft deep. The walls of the pit flare outward in lengthwise as the hopper deepens to lessen the chance of any bridging by the salt. The pit is 15 ft long at the base. The hopper walls taper inward at the base, lessening the width of the pit as it feeds a dual screw conveyor. Hopper capacity is estimated at 52,000 lb of salt or about 15% more than nominal load of the semi-trailer.

Grating will be provided over the hopper to prevent a fall hazard and too capture any large clumps of salt. Curbing will be provided around the hopper opening and the area around the hopper will be sloped to minimize the chance of rain or other contaminant from getting in the pit. The width of the hopper opening was designed to allow a truck to straddle the pit. The length was designed to allow a semi with a 9 ft hopper bottom to discharge without having to position the discharge precisely over the pit.

A Dual Screw Conveying system is located at the base of the receiving pit. This conveyor is designed to move salt from the hopper into a tubular chain conveying system that will transport it to the storage silo. The screws are to be counter-rotating and are to be 16-18 ft long. The action of the screw conveyor will aid in breaking up any clumps of salt prior to its future use in the process. The screw conveyor will be sized to unload the salt from up to 4 trucks per hour (180,000 lb/hr). It will have a variable speed drive to allow its speed to be matched to the tubular drag chain system described below.

**Tubular Drag Chain Conveying System**

A Tubular Drag Chain Conveying System is designed to transport salt through a series of individual conveying loops, from the base of the salt receiving pit and from the salt storage silo to the brine saturation pits, in a closed manner. The system consists of disks being dragged by chain through a tube. Salt is fed into the areas between the disks and is discharged by gravity either at drive stations or though air operated drop bottom valves. Following discharge, the disks are pulled back to the loading point to start the process again. Each loop contains, at a minimum, a drive unit which provides the motive force for the system and a chain tensioning station where the chain is kept taught to improve operations and decrease wear.
The system is designed to address two conveying rate requirements. A high capacity 10″ system is designed to move salt quickly from the salt receiving pit to the salt storage silo and a lower capacity 6″ system to move the salt from the base of the salt storage silo to the salt pits of the brine saturation system. The high capacity system can move 135,000 lb salt/hr (approximately 3 truck loads/hr) minimizing the time that trucks would need to wait for the receiving hopper to be emptied. The low capacity system is designed at 40,000 lb salt/hr. This is slightly higher than the maximum salt usage rate at full capacity to allow the ability to catch up should salt loading into the saturation system be disrupted.

The high capacity portion of the conveying system consists of two conveying loops. The first loop is fed salt from the screw conveyor at the base of the receiving pit and lifts it approximately 77 feet to a point at which the salt is discharged into a second loop that carries the salt horizontally about 19 feet to the top of the salt storage silo where it is discharged.

The low capacity portion of the drag chain conveying system also consists of two conveying loops. The first loop is fed salt via a rotary valve at the base of the salt storage silo. The first loop carries the salt approximately 55’ from the base of the silo up a slight incline to a point where the salt is discharged into a second conveying loop. Here the salt is horizontally conveyed a distance of approximately 60’ over the salt pits of the brine saturation system where it is discharged via drop bottom valve to pits 1 and 2 or via the drive station to pit 3. The valves will be cycled so that the salt will be dropping onto salt in normal operations, thus eliminating any potential spikes of hardness caused by dropping a large amount of salt into the liquid of the salt pit.

The system is designed to be as closed as possible. Salt will remain inside the tubes during conveying and will enter and exit the system through chutes. To address concerns with corrosion and abrasion with salt, materials of construction are either stainless steel or polyurethane. The system can be expanded at a later date by adding additional length to existing loops or introducing other loops into the system.

**Salt Storage Silo**

A salt storage silo is included in the design and provides two functions. It provides approximately one day storage (86,000 lb) of dry salt from the trucks and provides a spot in the process which decouples the truck unloading rate from the process usage rate. The storage silo will be approximately 20’ in diameter by 30’ high (straight side) and have a dome roof and a 60 degree cone bottom. The tank will be constructed with FRP and built to API 650 standards.

Salt will be introduced into the storage silo via chute from the tubular chain conveyor. The salt silo is vented to the dust collector located at the Salt Unloading Building. Salt will discharged through a rotary valve at the base of the silo. A variable speed drive on the rotary valve allows the feed to be adjusted to the conveying rate into the salt pits. A level transmitter will be included with the silo to monitor salt levels. The silos will be designed with provisions for the use of a bin vibrator to help restore flow if it is disrupted for any reason.
Brine Saturation System

The Brine Saturation system provides a means of contacting dry feed salt with lean brine returning from the chlor-alkali system. Lean brine contains brine from the chlor-alkali cells, make-up water, and other recoverable wastes, are pumped to the brine saturation system from the chlor-alkali plant. Here, the NaCl concentration of the brine will be raised from approximately 165 g/L to 293 g/L. This is accomplished by flowing lean brine upward through a bed of salt in a salt pit. The brine saturates and overflows a weir into a saturated brine pit where it is pumped to the process. Salt is replenished in the salt pits using the conveying system described above. The design is based on a system used in other chlor-alkali designs.

The system consists of 3 adjacent salt pits separated from each other by walls and from a common saturated brine pit by a weir. The multiple salt pit design allows for one pit to be out of service for maintenance with minimal interruption to overall operations. A platform is located on three sides of the pit system providing operator access to the salt pits and to a platform running over the saturated brine pit. The pits are dug into the ground to a depth that places the top of the weir at ground level.

The entire system is as closed as possible to minimize the chance of cross contamination between the salt and brine and the surrounding chemical and cement plants. Open salt and saturated brine pits are covered by a roof. Salt is supplied to the pits via chute from the conveying system. Operator access to the system is by roof hatches over each salt pit and via a door and platform over the saturated brine pit. A hydrophobic filter will allow in and out breathing when the doors and hatches are closed.

The Brine Saturation System is to be constructed of materials resistant to salt based corrosion. Concrete used in the pit walls, floors, and weir, will be epoxy lined. Roofing and non-structural walls will be fiberglass. Platforms, walkways and stairs will be FRP.

Salt pits are bounded by exterior or dividing walls, a salt retaining wall, a weir, and the floor. The salt retaining wall is located near the back of the salt pit and is elevated 6’ from the pit floor. The retaining wall allows salt to be piled in the salt pit without spilling into the saturated brine pit. Salt will be fed into the system close to the retaining wall to maximize the amount of feed salt that can be stored in the system. During normal operations the salt level is above the brine level in the pits and salt will be dropping onto salt as previously described. The weir is located about 1’ beyond the salt retaining wall. During operation, saturated brine flows through the gap and over the weir to the saturated brine pit.

The pipe used to introduce lean brine into the bottom of the salt pit passes through this gap as well. Lean brine exits the pit through holes drilled in the pipe. At least 5 pipes of varying length will be used to distribute lean brine into the salt bed. Flow of lean brine through any of the pipes can be adjusted or stopped via manual valve. Additionally, deionized water may be introduced into the system to help dissolve any salt causing plugging in the system.
It is estimated that each of the three salt pits will hold approximately 284,000 lbs of salt when full. When all pits are full, enough salt should be present to meet the chlor-alkali plants full capacity demand for saturated brine for approximately 1 day. Salt level is monitored using a bob-style level gauge and can be inspected visually through either of two hatches provided for each salt pit.

The saturated brine pit is bounded by the weir, floor, and exterior walls. The back retaining wall extends 42” above ground level to protect against accidental falls. Liquid level in the saturated brine will be maintained at about 6’ by controlling the speed of the brine feed pump. The level will be alarmed and interlocked to prevent the pump from running dry.

Access to the top of the saturated brine pit will be provided by a platform that runs above the pit for the length of the brine saturation system.

**Brine Feed Pumps**

The brine feed pump provides motive force to move the saturated brine out of the brine pit and into the primary brine purification. The pump is sized for 230 gpm, approximately half the required flow of the chlor-alkali plant. It is anticipated that at least two of the three salt pits will be in operation at any given time. The pump is variable speed to allow the brine feed rate to be adjusted when the plant is running at less than full capacity. It will be Tefzel-lined or constructed of a corrosion resisting alloy.

A slip stream downstream of the pump is circulated through a coriolis-type flow meter to measure the saturated brine density and compute the salinity. When salinity of the brine is too high, lean brine is fed into the line to bring the salinity to the level required by the chlor-alkali plant. A PCV is located downstream of the pump to prevent it from dead-heading.

The pump is located at ground level will lift saturated brine from the brine pit. The pump will be self-priming to account for any gas in the system. To assist in priming the pump and in clean-out, de-ionized water can be used to flood the pipeline at the inlet of the pump.

**AREA 600 – Chlor-Alkali and Bleach Storage**

**General**

The equipment in this area includes:

- Chlor-Alkali Plant
- Bleach Storage Tanks Off Spec Bleach Storage Tank
- Bleach Loading Package
Chlor-Alkali Plant

The purpose of the chlor-alkali plant is to provide caustic (NaOH) as a 32 wt% solution for use in carbon capture, scrubbing, and other minor uses. Any caustic required for use within the chlor-alkali plant is stored within the chlor-alkali plant battery limit. Lean Brine is sent from the chlor-alkali plant to the Saturation Tanks in Area 500. Saturated Brine is sent from the Saturation Tanks to the chlor-alkali battery limit.

Sodium hydroxide is generated through electrolysis of sodium chloride brine in a membrane cell. This process is part of a packaged system. The package is to be purchased as an integrated system, including secondary brine treatment, HCl synthesis, chlorine scrubber, and bleach preparation. The packaging of the system in this fashion provides a well defined process boundary allowing definable and measurable performance guarantees for the package.

Saturated brine is fed through a number of purification steps to remove hardness and other trace components using flocculation, filtration, and ion exchange steps. Ultrapure saturated brine is fed into the anode side of the electrolysis cell where the chlorine ions are oxidized to chlorine. At the cathode side of the cell, water is reduced to hydrogen gas hence releasing hydroxide ions into solution. The ion exchange membrane installed between the anode and cathode compartment allows the sodium ions to pass to the cathode side where they react with the hydroxide ions to produce sodium hydroxide.

The overall reaction for the electrolysis of brine is:

\[ 2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow \text{Cl}_2 + \text{H}_2 + 2\text{NaOH} \]

Each membrane cell is capable of producing a specific quantity of sodium hydroxide, chlorine, and hydrogen from brine. The quantity varies depending on the electrical current density at which the cell operates; the higher the current density, the higher the throughput of the membrane cell. Conversely, the overall electrical consumption or efficiency of the chlor-alkali process is inversely proportional to the electrical density. Hence, the overall electrical consumption per pound of sodium hydroxide produced is lowered as the current density is lowered.

The cells are stored in three electrolyzers which include structural frames that will hold the cells as well all interconnecting piping, wiring, and instrumentation required for operation. Each individual electrolyzer has an independent transformer/rectifier feeding the cells at a specific operating electrical current density as defined by the process operation specification.

Hydrogen and chlorine are formed in the electrolysis process. Each gas is dispersed separately from the cell and fed to a common header for each of the electrolyzers. Hydrogen gas leaving the cells is saturated with water. The hydrogen is sent through a cooler where water is removed. Downstream of the cooler, a demister removes entrained moisture prior to introduction of the hydrogen to the HCl synthesis unit. Chlorine gas is similarly handled. The
saturated chlorine gas is cooled to remove water and passed through a demister prior to introduction to the HCl synthesis unit.

Hydrogen and chlorine from electrolysis are combined in the HCl synthesis process. The HCl synthesis process produces HCl by the combustion of wet chlorine gas with wet hydrogen gas reacting to produce HCl gas. The gas is absorbed in demineralized water to produce the desired concentration of HCl liquid acid. The HCl synthesis unit relies on a furnace and other components constructed of materials that are engineered specifically to resist the corrosive environment and high temperatures of the process.

The combustion reaction is:

\[ \text{Cl}_2 + \text{H}_2 \rightarrow 2\text{HCl} \text{ (gas)} \]

The reaction is highly exothermic and high flows of cooling water are required to maintain temperature.

In order to ensure complete reaction of the chlorine fed to the HCl synthesis unit in a safe environment, the reaction needs an excess of hydrogen. The practical limits of operation will require combustion with excess hydrogen. As the quantities of hydrogen and chlorine are fixed from the electrolysis process, the result is that some amount of chlorine must be bled from the feed of the HCl synthesis unit to allow for the excess hydrogen requirement. This excess chlorine is the feed for the bleach plant.

The gas leaving the absorber (containing mainly inert gasses, excess hydrogen, and some HCl vapor) is fed into the bottom of a scrubber. The gas passes through the scrubber countercurrent to the flow of absorption water fed from the top.

The HCl synthesis unit is available as a packaged unit including burner controls, burner, furnace, absorption unit, and scrubber. This package, because of its close coupling to the electrolysis unit, is being supplied by the chlor-alkali plant supplier.

Sodium hypochlorite (bleach) is produced by the reaction of the excess chlorine with additional caustic within the chlor-alkali plant. The bleach plant is also sized to handle the entire load of chlorine from the electrolyzers until the plant can be safely shut down. Bleach not meeting the proper specification will be sent to the chlor-alkali battery limit for storage until it can be worked back into the bleach product stream.

The caustic, hydrochloric acid, and bleach products are sent to storage tanks outside the chlor-alkali plant battery limit.

The chlor-alkali plant is producing demineralized water for use within the plant. All other utilities are provided to the chlor-alkali battery limits in quantities determined by the chlor-alkali plant vendor.

The chlor-alkali vendor process description contains the detailed description of operations within the chlor-alkali process.
**Bleach Storage Tanks**

Bleach from the chlor-alkali plant is sent to one of two bleach storage tanks, constructed with FRP. Each bleach tank has a capacity to hold 1.5 days of production capacity. The bleach storage tanks have a vent to the atmosphere. The bleach is pumped from the bleach storage tank with the bleach loading pump at 200 gpm under flow control to the Bleach Loading Package.

**Off-Spec Bleach Storage Tank**

If the bleach in the chlor-alkali plant does not meet specifications, the off-spec bleach is sent to the Off-Spec Bleach Storage Tank. The off-spec bleach tank has a capacity of 8,000 gallons and has a vent to the atmosphere. The off-spec bleach will be blended with bleach product in the chlor-alkali plant at a rate sufficient to maintain bleach product specifications. The off-spec bleach pump is sized to send off-spec bleach to the chlor-alkali plant at a maximum of 10 gpm.

**Bleach Loading Package**

The Bleach Loading Package contains all controls, platforms, and connections necessary for loading bleach into trucks at a maximum rate of 200 gpm.

**AREA 700 – HCl Storage**

**General**

The equipment in this area includes:

- HCl Storage Tanks
- HCl Scrubber
- HCl Rail Loading Package
- HCl Truck Loading Package

Hydrochloric acid (minimum 35.2 wt%) is produced within the chlor-alkali plant. The hydrochloric acid is sent to storage tanks outside the chlor-alkali plant battery limit. HCl required within the chlor-alkali plant is provided from a tank and pump with the chlor-alkali plant. An HCl scrubber is provided to treat the vent from the storage tanks and railcar vent during loading to meet emissions requirements.

**HCl Storage Tanks**

HCl from the chlor-alkali plant is sent to one of two storage tanks constructed of FRP. Each tank has a capacity to hold 1.5 days of production capacity. The HCl storage tanks have
vents which are routed to the HCl scrubber before being released to atmosphere. The HCl is loaded to railcars from the HCl storage tank with the HCl rail loading pump at 400 gpm under flow control to the HCl rail loading package. HCl to the railcars can be diluted with HCl rail dilution skid. The HCl is loaded to trucks from the HCl storage tank with the HCl truck loading pump at 200 gpm under flow control to the HCl Truck Loading Package. HCl to the trucks can be diluted with HCl truck dilution skid.

HCl Vapor Recovery

Vapor from HCl loading is collected and sent to the HCl Scrubber along with the vent from the HCl Storage Tanks. The system will be a vendor package using dilute caustic as a scrubbing medium. The scrubbed vapor will be vented to the atmosphere.

HCl Loading Packages

The HCl Rail Loading Package contains all controls, platforms, and connections necessary for loading HCl into railcars at 400 gpm. The HCl Truck Loading Package contains all controls, platforms, and connections necessary for loading HCl into trucks at 200 gpm.

AREA 800 – Caustic Storage

General

The equipment in this area includes:

- Caustic Storage Tanks
- Caustic Storage Pump
- Caustic Dilution Package
- Caustic Unloading Arm

Up to 32 wt% caustic soda is produced within the chlor-alkali plant. The caustic is sent to storage tanks outside the chlor-alkali plant battery limit. Caustic required within the chlor-alkali plant is provided from within the chlor-alkali plant battery limit.

Caustic Storage Tanks

Caustic from the chlor-alkali plant is sent to one of three caustic storage tanks. The total volume of the three tanks is sized to store 2 days of production capacity. The caustic storage tanks have a vent directly to the atmosphere. The caustic is pumped from the Caustic Storage Tank with caustic storage pump to the Caustic Dilution Package.
Caustic Dilution Package

Caustic from the Caustic Storage Pump is diluted from 32 wt% to 20 wt% in the Caustic Dilution Package using filter water from Area 300. The Caustic Dilution Package is a skid mounted unit complete with controls and a heat exchanger to remove the heat of dilution with cooling water. Dilute caustic is sent from the dilution package to the Carbonate Column in Area 200 and the Knockout Tank in Area 100 for scrubbing.

Caustic Unloading Arm

Caustic will be unloaded from trucks to the Caustic Storage Tanks via the Caustic Unloading Arm. Delivery of caustic is expected at startup for initial fill of the electrolyzers and/or operation of the downstream carbon capture equipment before the chlor-alkali plant comes online.

AREA 900 – Utilities

General

The equipment in this area includes:

- Cooling Tower
- Chiller
- Boiler Package
- Air Compressors, Receivers, Dryer
- Rental Nitrogen Package
- Fire Protection System
- Waste Water Tank

Cooling Tower Water System

The cooling tower water system distributes cooling water from the cooling tower to all users.

A three-cell, field erected, pre-engineered, cross flow design cooling tower designed for 83.5 MMBTU/hr and 8,500 gpm is provided to handle the required duty. The tower has mechanically induced draft fans and 15 mil PVC film fill with integral louvers and drift eliminators. The fans are protected with vibration sensors.

The cooling tower design is based on a return water temperature of 105°F (max of 120°F) and a supply temperature of 85°F. The supply pressure is 30 to 60 psig, and the design return pressure is 10 to 30 psig. Process water from a city water tie-in, controlled by level in the cooling tower basin, rejects from the chlor-alkali reverse osmosis (RO) system, and membrane filter water are used for make-up water. A chemical treatment system treats the system.
Three cooling water centrifugal pumps (each rated for 4250 GPM or 50% flow), located at the cooling tower, pump cooling water into the supply header. Temperature and pressure are measured in the supply header that delivers cooling water. A back pressure valve at the end of the supply header maintains pressure in the header.

Measurements of pH, temperature, pressure and conductivity are taken at the return header, near the cooling tower. On high levels of conductivity, some water will bleed off to the waste water tank.

Cooling water is used for the air compressors, chillers, sodium carbonate cooler, flue gas coolers, flue gas compressors, caustic dilution package, and the chlor-alkali package.

**Chilled Water System**

The chilled water system distributes chilled water from the chiller to all users.

The chilled water refrigeration system is a packaged chiller skid sized for 275 tons, is provided. The system is configured in a closed loop. There is an expansion tank that enables the system to accommodate the water expansion due to temperature rise when the system is down. There are temperature and level indications on the tank.

Two parallel circulation pumps (each rated for 620 GPM or 100% flow) pump the returning chilled water past temperature, flow, and pressure measurements to the chillers. Control of the returning chilled water through the chiller is by pressure control in the supply header. Users pull off the supply header and return the chilled water back to the return header. A chemical treatment system is employed to treat the system as the chilled water returns by the expansion tank and to the chilled water pumps.

The chiller design is based on a return water temperature of 55°F and supply temperature of 45°F. The supply pressure is approximately 60 psig, and the design return pressure is approximately 30 psig. Cooling water is available for use during winter months with the chillers down.

Users for chilled water are the flue gas cooler and compressors’ after coolers.

**Steam and Condensate System**

The steam and condensate return distribution area distributes steam from a natural gas-fired boiler to the chlor-alkali plant.

Natural gas obtained from the public utility company fuels the small packaged boiler that provides 50 psig steam for heating at start-up in the chlor-alkali plant. Natural gas also goes to the bicarbonate dryer package and the chlor-alkali back-up generator. All users have flow meters.
Deionized water make-up to the boiler is from the chlor-alkali plant. Boiler blow-down goes to a blow-down tank and is quenched by process water before continuing to the waste water tank.

**Compressed Air System**

The compressed air system distributes dry pressurized air to all users.

A compressed air package consist of three oil-free, two-stage rotary screw compressors sized for 650 scfm each (each at 50% of total flow requirement) is included for instrument air and general purpose air users. The compressors supply pressurized air to the plant air and instrument air receivers at a working pressure of 100 psig. A heatless desiccant dryer dries instrument air to a minus 40°F dew point before the air goes to users within the plant. A moisture separator removes water from the plant air.

The compressors have intercoolers, after coolers, control panels and control devices furnished with the equipment. The air dryer has pre-filters, coalescing filters and controls for a complete system.

Users of plant air include utility stations and the chlor-alkali package. Users of instrument air include all instruments within the facility.

**Potable and Process Water Systems**

The potable and process water systems area provides potable and process water to the plant.

The source of water for the plant is potable water from the city. After a tie-in from the city water line, the potable water splits into two lines, one for potable water and the other for process water. Each line has backflow prevention.

Process water distributes to the cooling tower, flue gas cooler, knock out tank, chlor-alkali package, blow-down tank, membrane filter permeate tank, and utility hose stations. Potable water goes to the chlor-alkali plant and other users such as eyewash stations, water fountains and restrooms.

**Nitrogen System**

A rental nitrogen system, which is comprised of a liquid nitrogen tank, filling pump, vaporizer, instrumentation, controls and electronic telemetering to remotely monitor liquid level in the tank, supplies the required nitrogen for purging in the chlor-alkali plant.

**Fire Protection**

A fire protection system supplies water to the sprinkler systems for various parts of the plant.
Non-Contact Waste Water System

The non-contact waste water system collects and holds non-contact waste water for treatment prior to release to the city sewer system.

A 50,000 gallon tank stores waste water from the chlor-alkali plant, membrane filter, cooling tower blow-down, and process waste pump. pH and temperature are measured in the tank. A pump at the tank, controlled by the DCS, sends the waste water past a flow transmitter to the Sanitary Sewer.

3.1.1 Mass and Energy Balance

Initial Process Flow Diagrams (44 drawings), approximately 110 P&IDs, and general site and building arrangement plans were issued by FB&D in Phase 1 as part of the project scope package. These PFDs show compositions, temperatures, pressure, mass flow rates, and enthalpies for the major process streams. An overall mass balance shown in Table 3.1 details the incoming raw materials and the products and outgoing waste streams.

The energy balance summary details each process area’s power consumption. The total plant power consumption at peak performance is shown at the bottom of the Power Requirements table (Table 3.2).
There were two overriding considerations in the choice of current major operating points. The first is the reaction chemistry and thermodynamics, which drive the carbon capture and maintain the stability of both the carbonate and bicarbonate bubble columns with regard to column pH, precipitate production, and crystal growth. The second major consideration is the flue gas conditioning, which facilitates adequate water condensation (to drive mercury removal) and maintains the column temperatures and solubility points for optimum efficiency. Much of the basics for the reaction chemistry can be found in readily available literature, some of which dates back to the late 1800s. This provided guidance on optimizing the reaction chemistry, defining operating parameters, and developing prototypes at the field test unit. These reactions and conditions were modeled in Aspen simulations, which confirmed the major operating parameters and allowed the design to be fine-tuned to the specific flue gas of the host site.

**Reaction Chemistry and Thermodynamics**

### Table 3.2 Power Requirements by Area

<table>
<thead>
<tr>
<th>Area Number</th>
<th>Area Name</th>
<th>Power Required (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>Flue Gas Preparation and Processing</td>
<td>180.8</td>
</tr>
<tr>
<td>200</td>
<td>CO2 Absorption Columns</td>
<td>7.8</td>
</tr>
<tr>
<td>300</td>
<td>Bicarbonate Crystallization, Separation, and Water Recovery</td>
<td>958.3</td>
</tr>
<tr>
<td>400</td>
<td>Sodium Bicarbonate Drying and Rail Load Out</td>
<td>237.6</td>
</tr>
<tr>
<td>500</td>
<td>Salt Unloading and Brine Saturation</td>
<td>138.6</td>
</tr>
<tr>
<td>600</td>
<td>Bleach Storage</td>
<td>14.4</td>
</tr>
<tr>
<td>600C</td>
<td>Chlor-Alkali Ancillary Equipment</td>
<td>358.6</td>
</tr>
<tr>
<td>700</td>
<td>HCl Storage</td>
<td>10.4</td>
</tr>
<tr>
<td>800</td>
<td>Caustic Storage</td>
<td>3.9</td>
</tr>
<tr>
<td>900</td>
<td>Utilities</td>
<td>788.2</td>
</tr>
<tr>
<td></td>
<td><strong>TOTAL BALANCE OF PLANT POWER REQUIREMENT</strong></td>
<td><strong>2698.6</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Area</th>
<th>Power Required (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balance of Plant</td>
<td>2.70</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>18.42</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>21.12</strong></td>
</tr>
</tbody>
</table>

3.1.2 Critical Parameters
\[
\text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} = 2\text{NaHCO}_3
\]

<table>
<thead>
<tr>
<th></th>
<th>kJ/mole @ 298K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta \text{H})</td>
<td>-91.7</td>
</tr>
<tr>
<td>(\Delta \text{S})</td>
<td>-0.22</td>
</tr>
<tr>
<td>(\Delta \text{G})</td>
<td>-27.36</td>
</tr>
</tbody>
</table>

\[
\text{CO}_2 + 2\text{NaOH} = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}
\]

<table>
<thead>
<tr>
<th></th>
<th>kJ/mole @ 298K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta \text{H})</td>
<td>-84.1</td>
</tr>
<tr>
<td>(\Delta \text{S})</td>
<td>-0.11</td>
</tr>
<tr>
<td>(\Delta \text{G})</td>
<td>-52.01</td>
</tr>
</tbody>
</table>

**Reaction Equilibrium**

In the absorption column, the acid/base reactions are much faster than gas dissolution equilibrium reactions. The absorption process proceeds as follows:

1. \(\text{CO}_2\) gas is dissolved by the water and forms carbonic acid \(\text{H}_2\text{CO}_3\).
2. \(\text{H}_2\text{CO}_3\) donates one proton \(\text{H}^+\) forming bicarbonate \(\text{HCO}_3^-\).
3. \(\text{HCO}_3^-\) donates one proton to form carbonate \(\text{CO}_3^{2-}\).

The absorption of the \(\text{CO}_2\) and the formation of carbonic acid (step 1) are very slow compared to the proton formation (steps 2 and 3).

The equilibrium constants for steps 1, 2 and 3 are well known and shown in Table 3.3.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Constant at 25°C **</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CO}_2\text{g} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3)</td>
<td>(K_R = 3.6)</td>
</tr>
<tr>
<td>(\text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+)</td>
<td>(K_1 = 6.73)</td>
</tr>
<tr>
<td>(\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+)</td>
<td>(K_2 = 10.25)</td>
</tr>
</tbody>
</table>

**Table 3.3 Equilibrium Constants for Carbonate System**

The equilibrium constants for the two \(\text{H}^+\) formation steps are:

\[
K_1 = \frac{\text{[HCO}_3^-\text{][H}^+\text{]}}{\text{[H}_2\text{CO}_3\text{]}} = 10^{-6.73} \quad (1)
\]
\[ K_2 = \frac{(\text{CO}_3^-)(\text{H}^+)}{\text{(HCO}_3^-)} = 10^{-10.25} \]  

At steady state operation the absorption column represents a closed system. In other words, the total concentration \( C_T \) of carbonate species (\( \text{H}_2\text{CO}_3, \text{HCO}_3^-, \text{CO}_3^- \)) in solution is constant.

\[ C_T = (\text{H}_2\text{CO}_3) + (\text{HCO}_3^-) + (\text{CO}_3^-) \]  

We can determine \( C_T \) in our absorption column experiments and solve equations (1), (2), and (3) simultaneously.

\[ \frac{(\text{H}_2\text{CO}_3)}{C_T} = \frac{1}{1 + K_1/(\text{H}^+) + K_1K_2/(\text{H}^+)^2} \]  

\[ \frac{(\text{HCO}_3^-)}{C_T} = \frac{1}{1 + (\text{H}^+)/K_1 + K_2/(\text{H}^+)} \]  

\[ \frac{(\text{CO}_3^-)}{C_T} = \frac{1}{1 + (\text{H}^+)/K_2 + (\text{H}^+)^2/K_1K_2} \]  

Often, pH is used instead of the (\( \text{H}^+ \)). The relationship between pH and hydrogen ion concentration is:

\[ \text{pH} = -\log_{10}(\text{H}^+) \]  

Table 3.4 shows the fraction of the carbonate species (\( \text{H}_2\text{CO}_3/C_T, \text{HCO}_3^-/C_T, \text{CO}_3^-/C_T \)) for the full range of pH values.
The results in Table 3.4 may also be presented graphically. These results were also modeled in Aspen and compared in a later section.

<table>
<thead>
<tr>
<th>pH</th>
<th>(H)</th>
<th>(H₂CO₃)/Cₜ</th>
<th>(HCO₃⁻)/Cₜ</th>
<th>(CO₃²⁻)/Cₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00E-01</td>
<td>1.000E+00</td>
<td>1.862E-06</td>
<td>1.047E-15</td>
</tr>
<tr>
<td>2</td>
<td>1.00E-02</td>
<td>1.000E+00</td>
<td>1.862E-05</td>
<td>1.047E-13</td>
</tr>
<tr>
<td>3</td>
<td>1.00E-03</td>
<td>9.998E-01</td>
<td>1.862E-04</td>
<td>1.047E-11</td>
</tr>
<tr>
<td>4</td>
<td>1.00E-04</td>
<td>9.981E-01</td>
<td>1.859E-03</td>
<td>1.045E-09</td>
</tr>
<tr>
<td>5</td>
<td>1.00E-05</td>
<td>9.817E-01</td>
<td>1.828E-02</td>
<td>1.028E-07</td>
</tr>
<tr>
<td>6</td>
<td>1.00E-06</td>
<td>8.430E-01</td>
<td>1.570E-01</td>
<td>8.827E-06</td>
</tr>
<tr>
<td>7</td>
<td>1.00E-07</td>
<td>3.493E-01</td>
<td>6.504E-01</td>
<td>3.657E-04</td>
</tr>
<tr>
<td>8</td>
<td>1.00E-08</td>
<td>5.070E-02</td>
<td>9.440E-01</td>
<td>5.308E-03</td>
</tr>
<tr>
<td>9</td>
<td>1.00E-09</td>
<td>5.059E-03</td>
<td>9.420E-01</td>
<td>5.297E-02</td>
</tr>
<tr>
<td>10</td>
<td>1.00E-10</td>
<td>3.436E-04</td>
<td>6.398E-01</td>
<td>3.598E-01</td>
</tr>
<tr>
<td>11</td>
<td>1.00E-11</td>
<td>8.108E-06</td>
<td>1.510E-01</td>
<td>8.490E-01</td>
</tr>
<tr>
<td>12</td>
<td>1.00E-12</td>
<td>9.383E-08</td>
<td>1.747E-02</td>
<td>9.825E-01</td>
</tr>
<tr>
<td>13</td>
<td>1.00E-13</td>
<td>9.533E-10</td>
<td>1.775E-03</td>
<td>9.982E-01</td>
</tr>
<tr>
<td>14</td>
<td>1.00E-14</td>
<td>9.548E-12</td>
<td>1.778E-04</td>
<td>9.998E-01</td>
</tr>
</tbody>
</table>

Table 3.4 pH vs. Carbonate Species Concentration

Figure 3.2 pH vs. Carbonate Species Concentration
All of the reactions are reversible. The engineering team has seen this many times when forming carbonate with a high-molarity, high-pH caustic solution and continuing to flow CO₂ through the column. Eventually, all the carbonate is converted to bicarbonate as H⁺ is added to the system.

In summary, the overall reactions are:

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^-
\]

If excess hydrogen is added to the system by continuing to flow CO₂ through the column, the equilibrium of all the reactions shown will be shifted to the left. If excess hydrogen is removed from the system by adding NaOH, the equilibrium reactions will be shifted right. Bicarbonate formation is maximized at a pH between 8 and 9.

**Mass Transfer Calculations**

For a packed column, the absorption of CO₂ with a caustic solution is liquid phase controlled. In the Skyonic bubble column, the absorption of CO₂ with a sodium carbonate solution is gas phase controlled. The general packed column design equation is:

\[
Z = \frac{G}{K_G A} \int_{Y_1}^{Y_2} \frac{dY}{1-Y}(Y-Y^*)
\]

Where:

\[Z = \text{height of packing (ft)}\]

\[K_G A = \text{mass transfer coefficient (s}^{-1})\]

\[G = \text{flue gas velocity (ft/sec)}\]

\[Y = \text{mole fraction of pollutant}\]

\[Y^* = \text{mole fraction of pollutant at equilibrium}\]

Equation (1) may be expressed as:

\[
Z = [\text{HTU}][\text{NTU}]
\]

Where:

\[\text{[HTU]} = \frac{G}{K_G A}; \quad \text{[NTU]} = \int_{Y_1}^{Y_2} \frac{dY}{1-Y}(Y-Y^*)\]

is the height of a transfer unit (ft)

and the number of transfer units respectively.
When the CO\(_2\) concentration is low and the equilibrium line is straight, the integral portion of equation (1) becomes:

\[
[\text{NTU}] = \ln \left( \frac{Y_1 - mX_2}{Y_2 - mX_2} \right) \left( 1 - \frac{mG_m}{L_m} \right) + \left( \frac{mG_m}{L_m} \right) 
\]

Equation (3)

Where:

\(Y_1\) = mole fraction of Inlet CO\(_2\)
\(m\) = slope of equilibrium line
\(X_2\) = mole fraction of CO\(_2\) entering scrubbing liquid
\(Y_2\) = mole fraction of Outlet CO\(_2\)
\(G_m\) = molar flow rate of gas (kg moles/hr)
\(L_m\) = molar flow rate of liquid (kg moles/hr)

If the CO\(_2\) is extremely soluble or a chemical reaction occurs the slope of the equilibrium line approaches zero. Equation (3) reduces to:

\[
\text{NTU} \sim \ln \left( \frac{Y_1}{Y_2} \right) 
\]

Equation (4)

Thus, the number of transfer units depends only on the inlet and outlet concentration.

**Solubility Data**

Figure 3.3 shows a graph of the solubility of sodium carbonate and bicarbonate systems. This data has been recreated both empirically and modeling in Aspen.
The precipitation “sweet spot” shown in the figure depicts the optimal water content and temperature to precipitate bicarbonate only from a mixed solution of carbonate and bicarbonate. This method takes advantage of the difference in saturation points at the operating temperature of 40°C. At 40°C, the bubble column has the widest difference between the bicarbonate saturation point at 11%, and the carbonate saturation point at 32%. When a saturated solution of carbonate is fully converted to bicarbonate, only 11% of the bicarbonate will remain in solution while the difference of 21% of pure sodium bicarbonate will precipitate. These conditions are ideal, of course, but by choosing an operating point at 40°C, excess water can be added to create a buffer to prevent carbonate precipitation caused by temperature upsets or water imbalances. Also noted in Figure 3.3, sodium carbonate decahydrate can form at the operating saturation points if the temperature is not maintained above 85°F. This hydrate formation was a problem at the field test unit when saturated solutions of carbonate were allowed to cool to room temperature. Carbonate solution must be stored in a heated container and all piping must be flushed after transfer to prevent decahydrate formation. The solution for the decahydrate problems at the field test unit does not satisfy hydrate prevention steps needed in the pilot plant, which will operate continuously. Heated tanks and heat traced piping allow the pilot plant to operate without the need to flush piping. Testing at the field test unit confirmed that hydrate
formation that does occur can simply be melted with heat traced piping. The optimum water content and temperature was modeled in Aspen using sensitivity analyses that will be explained in the following section.

**Operating Parameters**

After defining the process, much of the Aspen work focused on polishing minor operations, such as temperatures, % water, and % solids in the bubble column bottoms to reduce energy consumption and cooling requirements. A filtration system to concentrate the solution after the absorption process is used to recycle unreacted carbonate to form bicarbonate precipitate. Due to having the carbonate recycled to the bubble columns, parameter changes in the system cascade throughout the process; this was modeled with Aspen's iterative approach. For example, changes that affect the % solids in the bubble column also impact the upstream and downstream flows with the possibility of changing the required number of decanters and/or filtration units.

In some early testing, the occurrence of foaming during testing in the decanter and bubble column was a short-lived problem that did help inform the design. In fact, foaming occurs when hydrocarbons are present in the carbonate solution (introduced into the system from the purchased sodium carbonate solids in this case) fed to the bubble column. The team confirmed that foaming occurs only when making sodium bicarbonate from trona (mined carbonate). Foaming does not occur from the carbonate solution made from membrane grade NaOH, which is representative of the NaOH that will be produced (via chlor-alkali) in the SkyMine® process.

Skyonic personnel developed product/sector profiles to include product data sheets for sodium bicarbonate and began to establish a baseline of SkyMine-produced product for complete compositional assay and comparison to commercial product specifications. Product sample production and analysis will grow in frequency and sophistication in Phase 2.

### 3.2 RESEARCH and DEVELOPMENT

In order to corroborate the simulation data, Skyonic personnel used both internal capabilities and external laboratories in Phase 1. Skyonic relocated its on-site SkyMine® field test unit from the Big Brown Steam Electric Station in Fairfield, Texas to the plant host site (see Figure 3.4). Phase 1 experiments included Aspen model validation and process characterization relative to CO₂ absorption and low-energy dewatering methods. To help characterize and optimize the process, experiments were conducted that included varying bubble column conditions.

**3.2.1 Field Test Facility**

The field test unit move and installation was completed in Phase 1 within the planned budget and ahead of schedule. This unit was expanded/upgraded in the latter part of Phase 1 and
includes test columns with pressure control, pH sensors, sample points (for fluid samples), and test points (for gas samples). With this facility, staff members have collected additional field data to more fully characterize the emitted flue gas and various process conditions sufficient to allow model corroboration. These efforts, in conjunction with data obtained from outside laboratory facilities, have been used to refine process simulation, which has ultimately led to improvements in process and control.

Figure 3.4 SkyMine® Field Test Facility at Capitol Aggregates’ Cement Plant

3.2.1.1 Flue Gas Testing

The Skyonic Engineering team used the field test facility to fully characterize the flue gas at the pilot plant host site. The gas handling components of the field test unit are stainless steel to resist the corrosive condensates formed in the cooling process. An air cooled radiator is the first piece of equipment that the hot flue gas encounters. The flue gas is cooled from 253°F to 150°F. The flue gas is then piped underground through a 2” PVC pipe for a distance of approximately 100 yards to the test facility. The underground piping provides additional cooling to 70-100°F depending on the gas velocity through the pipe. The condensate that forms in the cooling system is drained to a low point and recovered for heavy metals testing and disposal. The conditioned flue gas is slightly pressurized with a blower and fed into the sparger of the packed bicarbonate column for absorption. Also, in the pilot scale unit a dilute mixture of caustic is sprayed into the flue gas stream to knock out SOx and NOx. There are future plans to add this to the field test unit.

The field test unit uses a Testo portable gas analyzer, which measures and records the inlet and outlet values of the parameters listed in Table 3.5.
3.2.1.2 Absorption Column Testing

The first generation of columns at the field test facility (Figure 3.5) included a packed carbonate column and packed bicarbonate column which produced a saturated solution of sodium bicarbonate. To generate precipitate, water was evaporated from the saturated bicarbonate solution until the bicarbonate component was beyond the saturation point. After extensive testing, the materials and energy required for evaporation after absorption was deemed unacceptable. Work began on replacing the packed bicarbonate column with a bubble column in March 2010.

<table>
<thead>
<tr>
<th>Component</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>Percent by vol (%)</td>
</tr>
<tr>
<td>Carbon Dioxide (CO₂)</td>
<td>Percent by vol (%)</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Percent by vol (%)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Percent by vol (%)</td>
</tr>
<tr>
<td>Carbon Monoxide (CO)</td>
<td>ppm</td>
</tr>
<tr>
<td>Sulfur Dioxide (SO₂)</td>
<td>ppm</td>
</tr>
<tr>
<td>NO</td>
<td>ppm</td>
</tr>
<tr>
<td>NO₂</td>
<td>ppm</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>ppb</td>
</tr>
<tr>
<td>Density</td>
<td>Lb/ft³</td>
</tr>
<tr>
<td>Temperature</td>
<td>°F</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>cuft/min</td>
</tr>
</tbody>
</table>

**Table 3.5 Flue Gas Composition Components**
The first generation field test unit demonstrated the CO₂ scrubbing process at the Capitol Aggregates plant using a four column system. Specifically, smaller, clear columns were used to identify process conditions that may facilitate a reduction in capital equipment cost for the plant. Furthermore, liquid distributors, designed by an industry leader, were included. The SkyMine® process reacts carbon dioxide with sodium hydroxide to form sodium bicarbonate. Experiments included varying gas flow rate and recirculation rate as well as sodium hydroxide feed concentration to optimize...
the process. These experiments improved process performance and the data was used to enhance the Aspen simulation where appropriate.

Tests were run in the first generation packed columns during 2009 and early 2010. The empirical data collected was compared to an identically scaled model in Aspen. Both the Aspen model and the field test unit were run in parallel. The first generation absorption process takes place in a series of packed columns with dimensions, materials and the internals of each column shown in Table 3.6.

<table>
<thead>
<tr>
<th></th>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
<th>Column 4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Length</strong></td>
<td>15 feet</td>
<td>5 ft</td>
<td>5 ft</td>
<td>5 ft</td>
</tr>
<tr>
<td><strong>Diameter</strong></td>
<td>33 Inches</td>
<td>33 in</td>
<td>17 in</td>
<td>17 in</td>
</tr>
<tr>
<td><strong>Packing Height</strong></td>
<td>12 feet</td>
<td>3 ft</td>
<td>3 ft</td>
<td>3 ft</td>
</tr>
<tr>
<td><strong>Material</strong></td>
<td>Poly Pro - Black</td>
<td>Poly Pro - Black</td>
<td>PVC - clear</td>
<td>PVC - clear</td>
</tr>
</tbody>
</table>

**Table 3.6 Packed Column Dimensions**

Each of the four columns contains a liquid distributor, a flue gas sparger, and packing. The packing material is PVDF Lantec Nupac #2. The ΔP across the column is approximately 5 inches H₂O. Table 3.7 shows the packing specifications from the vendor.

<table>
<thead>
<tr>
<th></th>
<th>#2 NUPAC®</th>
<th>#4 NUPAC®</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nominal Size</strong></td>
<td>2.5 in</td>
<td>4.5 in</td>
</tr>
<tr>
<td><strong>Void Fraction</strong></td>
<td>90.9%</td>
<td>94.2%</td>
</tr>
<tr>
<td><strong>Geometric Surface Area</strong></td>
<td>55 ft²/ft³</td>
<td>40 ft²/ft³</td>
</tr>
<tr>
<td><strong>Weight - polypropylene</strong></td>
<td>5.1 lbs/ft³</td>
<td>3.1 lbs/ft³</td>
</tr>
<tr>
<td><strong>Weight - PVDF</strong></td>
<td>9.0 lbs/ft³</td>
<td>6.3 lbs/ft³</td>
</tr>
<tr>
<td><strong>Number of Pieces</strong></td>
<td>125 /ft³</td>
<td>22 /ft³</td>
</tr>
<tr>
<td><strong>Packing Factor</strong></td>
<td>16 /ft</td>
<td>8 /ft</td>
</tr>
</tbody>
</table>

**Table 3.7 Nupac Packing Specifications**
Materials and Methods

Flue gas is fed into four individual packed columns in series with incoming gas entering at the bottom of column 1 and exiting out of the top of column 4. Incoming gas is cooled to approximately 35°C prior to entering the first column. A small blower is used to build up pressure to overcome pressure drop of the packing and liquid level in the columns. In all columns, gas enters at the bottom and exits out through the top and liquid flow is countercurrent. Each column has a recirculation pump, metering pump, pH sensors, sample point (for fluid samples), test point (for gas samples), drip tray (for fluid distribution), and a flow indicator and a manual valve to control recirculation flow.

Sodium hydroxide is mixed in a stainless steel tank at varying concentrations. The sodium hydroxide feed flows counter to the flow of gas, entering column 4 and exiting column 1 into a product drum. Metering pumps regulate the liquid transfer into, between, and exiting the columns. Figure 3.6 shows the detailed instrument and flow diagram.

Future Testing

As stated above, the first generation column system is being replaced with a carbonate column followed by a bubble column system that has proven in Aspen to be more material and energy efficient. Though the two-packed-columns system is no longer the plan for the pilot plant, all of the information collected from the first
generation field test unit columns was factored into the design of the resulting bubble column system for the pilot plant.

Construction of the bubble column (Figure 3.7) began in August of 2010, and will provide the field test unit with the capability to test and characterize the formation of bicarbonate crystals from a carbonate solution.

The column was constructed with clear PVC to allow the team to visualize the crystallization and precipitation of the bicarbonate. Additionally, the clear column was beneficial in determining the amount of mixing and minimizing precipitate settling. An Aspen model of the field test unit bubble column was created to run in parallel with the prototype bubble column. This Aspen model will compare capture efficiencies, reaction rates, solids formation and heat of reaction to empirical data, much like the simulation and field work comparisons of the first generation columns. The Aspen model will ultimately be used to validate the scale-up for the pilot plant.
3.2.2 Process Modeling & Characterization

The individual unit operations of the SkyMine® process are largely proven processes, and much of the equipment used in a SkyMine® plant is of standard issue and capacity. Though complex, the multi-phase CO₂/bicarbonate recovery system can operate over a range of conditions that have trade-offs between recovery, efficiency, energy, and capital expense. These sets of conditions have been exhaustively tested through interpolation/extrapolation of empirical data and predictive modeling based on reaction rate kinetics and equilibrium models. Aspen modeling (see Figure 3.8) enabled the team to both evaluate and validate several design concepts used to capture CO₂ and purify products generated by the process, to develop cost sensitivity analyses related to key process variables, and to evaluate alternative modes of operation in terms of power needs and process operational efficiency. In the model, the stream and equipment names match those in the PFDs for a smooth transaction when porting the model into the mass balance. The Aspen modeling software used included Aspen Plus 7.1 and Aspen Heat Exchanger Design 7.1.

Figure 3.8 Aspen-generated Flow Sheet
3.2.2.1 Flue Gas Conditioning

Operation of the front-end flue gas heat exchanger has a ripple effect throughout the process. The flue gas conditioning process was modeled using the flue gas data collected on site as well as the host site’s 2009 emissions data as the inlet stream to the system. The simulation includes all major individual pieces of equipment. The heated flue gas is transferred through the system using a blower followed by a heat exchanger with three cooling mediums. This was modeled using a pressure changer to increase the pressure to 30 inches of H₂O and three individual heat exchangers, with hot water, cooling tower water, and chilled water, respectively. The heat exchangers were ported to the Aspen Heat exchanger design program to produce data sheets for the vendors. The exchangers were modeled using the Aspen Aerotran calculation method. Following the heat exchangers, dilute caustic is added using an Aspen mixer block to knock out SOx and NOx from the flue gas. The condensate and caustic spray down is separated from the gas stream using a flash tank, which is accomplished in Aspen using a separator flash block. A close-up of this section of the flue gas conditioning Aspen flow sheet is shown below in Figure 3.9.

![Flue Gas Conditioning in Aspen 7.1](image)

Figure 3.9 Flue Gas Conditioning in Aspen 7.1

3.2.2.2 CO₂ Absorption

A range of flue gas temperatures, between 77°F and 150°F was modeled as feeds to the carbonate columns. As verified in the equilibrium data, the model shows that at higher carbonate column operating temperatures it was necessary to add excess water to the caustic to avoid carbonate precipitation. Also, the higher carbonate bottoms temperature draws the need for additional cooling of the saturated carbonate stream, which feeds the bubble column. This can otherwise be offset by a colder flue gas feed to the bubble column to maintain its desired operating conditions (e.g. additional chiller load) thereby negating any benefit derived from the higher temp.
Using this concept, the Aspen model allowed the cooling duties to be balanced to use chilled water only where absolutely necessary, thus reducing the overall energy balance.

The conditioned flue gas leaves the separator flash block and is divided into four streams using a stream split block. The split block represents the duct valves that will divide the flue gas equally to the separate absorption trains. Figure 3.10 shows the section of the Aspen flow sheet that models the carbon capture.

![Figure 3.10 CO₂ Absorption in Aspen](image)

As noted in the figure, flue gas enters the base of the carbonate column in stream 251 at a temperature of 104°F. The carbonate column is modeled using a RadFrac block with no condenser or reboiler duty. In the block, the column dimensions, packing type, efficiency, stream inlet/outlet locations, and pressure drop are specified using information from vendors and empirical data. The carbonate column bottoms stream is a saturated carbonate solution. The carbonate column block calculates the heat of reaction which is evident by the temperature increase in stream 252. This stream is transferred to a mix tank block with a pressure changer pump block where the carbonate from both trains is combined. A single heat exchanger, modeled with a shell and tube block, cools the carbonate stream 354 to a suitable temperature before entering the bubble column.

As seen in the lower half of Figure 3.10, stream 165 splits off of the flue gas header to feed the compressor. This is also modeled with a pressure changer block where efficiency and outlet pressure are specified. The compressor efficiency was specified by the vendor. The heat of compression of the flue gas increases the stream
temperature and must be cooled again, modeled by a series of heat exchanger blocks. The flue gas is cooled to a temperature lower than the compressor inlet resulting in some additional condensate formation. This is separated from the gas stream similarly to the flash separator block in the flue gas conditioning section. Stream 305 exits the flash block and enters the bottom of the bubble column. The bubble column is modeled with Aspen’s solids crystallizer block. The formation of bicarbonate crystals is effectively modeled concurring with the solubility data in the earlier section.

3.2.2.3 Dewatering, Filtration and Drying

As shown on the left side of Figure 3.11, each of the bubble columns outlet slurries are mixed in an agitated mixer block. This stream is transferred to the decanter which is modeled using a solids separator block. The moisture level and solids fraction are inputs to this block and were based on information provided by the decanter vendors. The centrate, stream 310, is transferred using a pressure changer pump block to the membrane filtration unit, modeled with a component separator block. The inputs for this block, including efficiency and water recovery, were based on empirical data from the vendor.

Figure 3.11 Dewatering, Filtration, and Drying in Aspen

At the bottom right of figure 3.11, the dryer is simulated using a combustion block followed by a reactor block. Air and natural gas feed the burner block and the heated air and products of combustion stream enter the dryer block. Stream 362, which is the
wet bicarbonate, enters the dryer with the hot air stream from the burner to result in the evaporation of the water from the solids without reaching decomposition temperatures of the product. A full scale dryer test was performed at the vendor’s test facility where the empirical data was used to calculate the natural gas consumption and blower energy.

3.2.3 Process Control

The field test unit is equipped with gas analyzers, pH probes, temperature and pressure sensors, etc. Excessive instrumentation is fairly typical for equipment in field test units. This allowed the team to accurately design the pilot plant by specifying only the necessary instrumentation and controls as validated by field testing.

The pilot plant is designed to be operated from a central control room, located in the chlor-alkali process facility, via a distributed control system. The supplier of the overall control system must be coordinated with the chlor-alkali system supplier.

3.2.4 Vendor Testing

Heavy metals removal is one of the primary functions of the Skyonic process. This removal process is highly dependent on the composition of the host site’s flue gas. In this case, the condensate was collected from the flue gas on site and sent out to a third party laboratory for analysis. This analysis was necessary to determine what filtration steps would sufficiently remove the heavy metals from the condensate. A follow up flue gas condensate test was also performed and was analyzed by ICP-OES (inductively coupled plasma optical emission spectrometer) for metals composition, with a focus on mercury. Results were calculated to units of ppb. Mercury concentration is very low, just a little higher than the detection limit.

Follow up testing in Phase 2 will include lab scale filtration of a condensate sample from the host site.

During Phase 1 the engineering team evaluated multiple methods of solid/liquid separation. Initially, a lab scale centrifuge was used for this purpose. Subsequently the team settled on a process that involves a decanter operation followed by membrane filtration and a subsequent drying step to more closely model the pilot plant design. Decanters are utilized as the first dewatering unit process downstream of the bubble column to separate the bicarbonate slurry into liquids and solids. Three vendors were chosen to test their decanters with bicarbonate provided by Skyonic. The tests were designed to confirm equipment model, separation efficiency, and number of decanters as recommended by each vendor.

The use of commercially available membrane filtration at high pressure to remove water from a saturated solution of sodium carbonate and bicarbonate was tested at small/lab scale. The testing focused on water recovery and minimizing membrane plugging due to precipitation. Multiple membrane pore sizes and materials were tested before the vendor settled on a recommendation. A production prototype unit was designed and will be tested in the spring of 2011 as a scale up vehicle for the pilot plant.
The process for drying the sodium bicarbonate product is highly temperature sensitive as bicarbonate decomposes at 160°F. To prevent decomposition and agglomeration, an agitated flash drying method was chosen. This method allowed particles to dry without exposure to high temperatures and the agitation prevented agglomeration of crystals. Phase 1 testing focused on identifying in-feed material moisture content, the necessity of a partial pressure of CO₂, and validation of the drying temperature that would result in highest product purity with the least energy consumption. Agglomeration and temperature issues were confirmed/validated when tested on a production dryer during vendor testing.

After the drying process, the bicarbonate product must be transported to the railcar load out station. This is located 900 feet west of the dryer so pneumatic conveying was the best option. Testing for pneumatic conveying is not available on a small scale. The vendor testing was performed at its test facility for distances of over 1000ft.

### 3.3 FACILITY/SITE PLANNING

Site planning was advanced in Phase 1 through a number meetings and subject matter expert review of civil engineering issues to include boundary definition, roadways, rail design, utilities, and environmental requirements. Roadway issues, including ingress and egress, capacity, functionality (turn-around, etc.), traffic scheme, proximity to rail and OTR vehicle stations, public road, entrance design/location, and construction were addressed with host site officials, and civil consultants under contract with Skyonic. Construction and fencing arrangements were addressed in a manner to satisfy OSHA and MSHA requirements.

The civil consultants also began work on a civil survey, topographical plan, and geotechnical study. The team evaluated a number of rail loading/unloading schemes.

Discussions with host site officials and local electric utility (CPS) officials took place to define and negotiate electrical substation requirements. Project team members also met with officials of the San Antonio Water System (SAWS) on water requirements, sewage and storm water design, fire logistics, and permitting procedures.

#### 3.3.1 Basis of Design

The SkyMine® Process is a unique, patented process designed to remove carbon dioxide from a gaseous waste stream, convert the carbon dioxide to a mineralized carbon product, and produce valuable chemical byproducts. The SkyMine® process can remove over 90 percent of the carbon dioxide from a flue gas stream.

The design of the SkyMine® process is based on receiving carbon dioxide-laden flue gas from an existing stationary source (the Capitol Aggregates cement factory in San Antonio, Texas). The equipment will be designed to meet the production requirements based on operating 350 days per year. The plant is expected to operate continuously except for scheduled maintenance shutdowns, or shutdowns caused by external factors (utilities, feedstock, extreme weather, etc.) and is designed to produce NaOH as feedstock for the decarbonation process used to capture 75,000 tonnes/yr of CO₂ from a flue gas stream. Upon capture of a slipstream
of waste flue gas, the SkyMine® process will condition it, and ultimately convert significant portions of the carbon dioxide into valuable, marketable products.

The flue gas stream will be cooled, resulting in condensation of moisture from the gas. This condensate will capture a number of environmentally undesirable elements that can be disposed of or reprocessed. The cooled gas is then reacted with sodium hydroxide. This reaction ultimately yields a high purity sodium bicarbonate crystal product suitable for sale.

The sodium hydroxide is produced, on site, through an electrolysis process requiring a NaCl brine feedstock. The electrolysis process converts the brine into three products: sodium hydroxide (for the flue gas reaction), hydrogen and chlorine. The hydrogen and chlorine are then burned to produce high purity hydrochloric acid.

In general, the SkyMine® process has two feed requirements (carbon dioxide laden flue gas and brine) and produces three products (hydrochloric acid, sodium bicarbonate crystals, and bleach).

3.3.2 Electrical Power Design

A detailed electrical power design was completed in Phase 1. This specification establishes the guidelines for the design of a safe, economical and reliable electrical power system and addresses all aspects of power load and distribution, codes and standards, equipment, grounding, back up, and safety.

3.3.3 Scope of Work (EPC)

The project scope is defined, physically, by the property outline illustrated in the overall Site Plan. In general, the project interface points are located at the fence line depicted on the site plan with clarifications spelled out in the detailed Scope of Work documents.

The EPC contractor will provide engineering, procurement, construction management services and support staff, field supervision and staff, labor, described materials and equipment, construction equipment, tools and supplies for the Project as described in contract documents and exhibits.

3.3.4 Site/Plant Layout

The project team worked with host site officials and project subcontractors to develop a detailed site plan. The pilot plant layout encompasses an area of approximately four acres on the Capitol Aggregates Cement Plant site.
A civil engineering firm has been engaged for the project and will craft a civil preparation plan. Elements of the plan will include a site topographical drawing, a grading plan, site drainage, fire protection, tree ordinance compliance, and assistance with permitting in San Antonio.

When the site layout is updated to reflect chlor-alkali boundaries, the civil and railroad engineering design work associated with grading and traffic flow will proceed. The preliminary development of site will be discussed with the City of San Antonio Development Board in early December 2010 in order to prepare both the City and Skyonic for the project requirements.

Civil Engineering grading drawings are anticipated to be completed in February 2011. Railroad design drawings, which will be submitted to Union Pacific for comment, are also scheduled to be completed in February 2011.

A contract was issued to design the rail traffic scenario and to integrate optimally with the existing Capitol Aggregates (CA) yard. The contractor will provide construction-quality drawings suitable for use in obtaining competitive quotes, and will provide completed drawings to Union Pacific officials for review/comment/approval prior to construction activity.
The project team will continue to work with the host site to identify and mark boundaries. A construction and fencing scheme that will address OSHA/MSHA requirements will be completed prior to construction.

3.4 EQUIPMENT

Specific process equipment identification and validation was augmented by visits to industrial plants to view, first hand, identical or similar equipment at full scale operation. The project team also held meetings with personnel from the various vendors’ equipment user bases. Additionally, material handling equipment for product conveyance (at varying rates and distances) and storage was also evaluated. Detailed bid packages and quotes were solicited from qualified vendors and evaluated by project team members for performance, operating and capital costs, and sustainability.

3.5 ENVIRONMENTAL/NEPA PLANNING

Under contract with Skyonic Corporation, qualified environmental consultants helped to develop a comprehensive environmental permitting strategy and assisted in producing the data necessary for DOE to execute its responsibilities under NEPA.

Environmental permitting requirements have been identified and no major permits are required. Due to the nature and location of the project and the small amounts of emissions, all permits may be completed through the permit-by-rule process. All permitting activities can be completed prior to construction within the current project timeline.

Skyonic, together with environmental consultants and legal counsel, reviewed applicable regulations and met with the Texas Commission on Environmental Quality (TCEQ) to determine environmental permit requirements, which are summarized table below:

<table>
<thead>
<tr>
<th>PBR Number</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>106.144</td>
<td>Bulk Mineral Handling</td>
</tr>
<tr>
<td>106.183</td>
<td>Boilers, Heaters, and Other Combustion Devices</td>
</tr>
<tr>
<td>106.261</td>
<td>Facilities (Emission Limitations)</td>
</tr>
<tr>
<td>106.262</td>
<td>Facilities (Emission and Distance Limitations)</td>
</tr>
<tr>
<td>106.371</td>
<td>Cooling Water Units</td>
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<tr>
<td>106.472</td>
<td>Organic and Inorganic Liquid Loading and Unloading</td>
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</tbody>
</table>

Table 3.8 Permits By Rule

Other permits / notices identified that are to be developed and submitted during the final design, subsequent construction, or startup process are listed in the table below:
<table>
<thead>
<tr>
<th>Item</th>
<th>Title</th>
<th>Statute or Regulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industrial Storm Water Releases</td>
<td>TPDES Multi-Sector General Permit - Storm Water Discharges - Industrial Activity</td>
<td>40 CFR Part 122, Subpart B Texas Water Code, Section 26.040</td>
</tr>
<tr>
<td>Wastewater Pretreatment Permit</td>
<td>San Antonio Water System (SAWS) Pretreatment Permit</td>
<td>San Antonio, Texas, Code of Ordinances, Sec. 34-471 – 484,</td>
</tr>
<tr>
<td>Solid Waste Disposal</td>
<td>Solid Waste Management, Disposal of Nonhazardous or Hazardous Industrial Solid Waste</td>
<td>30 TAC Ch. 335</td>
</tr>
<tr>
<td>Presence of chlorine at or above the Threshold Planning Quantity (TPQ)</td>
<td>Emergency Planning and Community Right-to-Know Act (EPCRA), also known as Title III of the Superfund Amendments and Reauthorization Act (SARA)</td>
<td>EPCRA Sections 302, 311, 312</td>
</tr>
<tr>
<td>Release of chlorine above the Reportable Quantity (RQ) of 10 pounds or more</td>
<td>Emergency Planning and Community Right-to-Know Act (EPCRA), also known as Title III of the Superfund Amendments and Reauthorization Act (SARA)</td>
<td>EPCRA Section 304, 40 CFR Part 302</td>
</tr>
<tr>
<td>Manufacture or process more than 25,000 pounds or use more than 10,000 pounds of chlorine</td>
<td>EPCRA Section 313, Toxic Release Inventory (TRI) Reporting</td>
<td>40 CFR Part 372</td>
</tr>
</tbody>
</table>

Table 3.9 Additional Permit Requirements

Further, and as required by the NEPA process, Skyonic completed a comprehensive Environmental Information Volume (EIV) and submitted it as part of the Phase 2 Application package. Information from the environmental sections is included in this section.

### 3.5.1 Proposed Project

The concentration of CO$_2$ in the atmosphere has increased 17.4 percent over the past 60 years (Keeling and Whorf, 2002). The Intergovernmental Panel on Climate Change (2001) has concluded that these changes result principally from accumulation of anthropogenic CO$_2$ emitted to the atmosphere as a result of changing land use patterns and combustion of fossil fuels, such as coal, oil, and natural gas, to produce energy; the current project addresses an industrial means of capturing and sequestering carbon dioxide in a mineral form as a means of reducing the emissions about which this report is concerned. Predictions of global energy use in the next century suggest that anthropogenic carbon emissions will continue to increase, resulting in continued rising atmospheric concentrations of CO$_2$ unless major changes are made in the way we produce and use energy (DOE, 1999, p 1-1).
Uncertainty remains in predicting the effects of this change in composition of the atmosphere. However, there is significant risk that continued increase in atmospheric concentrations could force changes in global climate, which may have a variety of serious consequences (see U.S. Climate Change Science Program / U.S. Global Change Research, 2003 http://www.usgcrp.gov/usgcrp/nacc/education/default.htm for regional summaries or the Intergovernmental Panel on Climate Change http://www.ipcc.ch/, 2003).

The overall objective of this pilot project is for Skyonic to test the feasibility of innovative concepts and processes for the beneficial, economic use of CO₂ captured from otherwise emitted flue gas, and so doing with job-creating profitable, low carbon manufacturing. The SkyMine® technology accomplishes this by removing CO₂ from industrial waste streams through co-generation of carbonate and/or bicarbonate materials and converting it to products with beneficial use. The bicarbonates produced from the mineralization process can be sold and used for a variety of purposes such as in animal feedstock, to grow algae/biomass, and others. With technology perfected in field trial facilities, the first pilot-scale SkyMine® plant will harvest CO₂ from flue gas at the Capitol Aggregates cement manufacturing plant in San Antonio, Texas.

The SkyMine® process developed by Skyonic Corporation utilizes basic chemical reactions to effectively remove over 90 percent of the CO₂ from the flue gas of a large combustion source. Figure 3.13 is a simple flow diagram to illustrate the major components of the process for the pilot SkyMine® Project. The following is a brief description of that process:

- A portion of the flue gas from the Capitol Aggregates coal-fired drying kiln will be first routed through heat exchanges to condense the moisture in the emissions. Cooling towers will be used reduce the temperature of the cooling water used in the heat exchangers. The condensed process water is treated, drained or returned to use. It will be filtered through activated carbon to remove impurities and recycled for later use in the process. The spent carbon filters are periodically replaced and properly disposed of as solid waste.

- Salt (sodium chloride) is brought in by truck, dissolved in a simple brining operation, and treated to remove impurities, such as sodium sulfate, which could interfere with the SkyMine process. Some wastewater is generated and pretreated before being discharged into the municipal sewage treatment system. A baghouse is used to control the small amount of particulate emissions that may result from the dry salt handling.

- The brine is subjected to an electrochemical process that separates it into sodium hydroxide, chlorine gas, and hydrogen. The sodium hydroxide is transferred to storage tanks and the chlorine and hydrogen are immediately combined and sold as HCl.

- The sodium hydroxide is used as the absorption media in the carbon dioxide scrubber towers. The treated flue gas is bubbled through the sodium hydroxide where it reacts with the carbon dioxide to form sodium bicarbonate which precipitates as a solid. This absorption process also removes all of the sulfur dioxide and acid gases, as well as small amounts of nitrogen oxides, resulting in a significant reduction in overall Capitol Aggregates’ flue gas emissions.
• The sodium bicarbonate is further treated with additional CO₂ from the flue gas stream and dried. Final product is transferred through pneumatic pipes to railcars or tank trucks for shipment to customers. A baghouse is used to control the small amount of particulate emissions that may occur. The emissions from the natural gas heater and a small amount of flue gas are also released through the baghouse.

• The chlorine and hydrogen generated by the electrochemical process is combined with water to produce hydrochloric acid which is also stored and transferred by railcar or tank truck to customers. A wet scrubber is used to control the small amount of vapor produced during loading operations.

• A small amount of the chlorine is also combined with sodium hydroxide to form sodium hypochlorite (bleach) which is also stored and transferred to customers, primarily through tank trucks.
Figure 3.13 SkyMine® Process Flow Diagram
If determined by this pilot project to be economically feasible, the SkyMine® technology will also establish a practical alternative for reducing CO₂ emissions in areas where geologic storage, the predominant competing CO₂ sequestration technology, is not an optimal solution. In fact, the U.S. Geological Survey (USGS) has identified a significant “geospatial mismatch between size of storage needed for sequestration projects and the location of large sources of CO₂.” (USGS 2008) Additionally, the SkyMine® process avoids other potential problems with the geologic injection methods such as the possible disturbance to regional ground-water flow systems, contamination of drinking water supplies, and other potential impacts to ecosystems.

The proposed project area is approximately 4 acres with surrounding access collocated on the 600-acre property of the Capitol Aggregates cement manufacturing plant in San Antonio, Texas, approximately 2.5 miles north of Interstate Highway 410, 2.0 miles west of Interstate Highway 35, 4.0 miles east of Texas Highway 281, and 3.3 miles south of Texas Highway 1604. All activities related to the commercial operations at the project site will be authorized by the Texas Commission on Environmental Quality (TCEQ) and the San Antonio Water System (SAWS).

Capitol Aggregates will provide the following contributions to the project:

- Commitments, operational coordination, and corporate-level involvement necessary to make the project feasible in the timeframe set forth in the DOE Funding Opportunity Announcement;
- Long-term lease of approximately 5 acres for the construction and operation of SkyMine® plant units and associated rail spurs for the duration of the project;
- Supply of process emissions stream from its main stack into SkyMine® absorption (scrubber) tower;
- Connection to its municipal sewage collection lines to accept domestic wastewater from Skyonic offices and other buildings;
- Access to connections for the discharge of SkyMine® process discharge water into the San Antonio Water System (SAWS) collection system;
- Access to connections to the San Antonio Water System (SAWS) for process and cooling water supply; and
- Coordination with Skyonic on any changes to its operations that may impact or alter the SkyMine® process or result in additional constituents that may need to be addressed.

City Public Services (CPS), the public electricity provider for San Antonio, will provide electricity to the SkyMine® facilities.

The San Antonio Water System (SAWS), the public water and wastewater service provider for San Antonio, is prepared to supply fresh water to the site for process and potable use and will accept industrial wastewater that has satisfied its pretreatment requirements into its Publicly Owned Treatment Works (POTW).
Table 3.10 provides an overview of the major project milestones for the SkyMine® project.

<table>
<thead>
<tr>
<th>Major Milestones</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engineering/Control Estimate Preparation</td>
</tr>
<tr>
<td>Detailed Design</td>
</tr>
<tr>
<td>Site Preparation</td>
</tr>
<tr>
<td>Underground Piping, Utilities, Foundations</td>
</tr>
<tr>
<td>Building Erection, Electrical, Plumbing, Interior Systems</td>
</tr>
<tr>
<td>Process Equipment, Utility, Service System Installation</td>
</tr>
<tr>
<td>Start-ups and Commissioning</td>
</tr>
</tbody>
</table>

Table 3.10 SkyMine® Project Milestones
Figure 3.14
Topographic Map of SkyMine® Project Area
Bexar County, Texas
Figure 3.15
Aerial (Google Earth) Map of SkyMine® Project Area
Bexar County, Texas
3.5.2 Impetus for Action

In the June 2009 Funding Opportunity Announcement (DE-FOA-0000015) for Carbon Capture and Sequestration from Industrial Sources and Innovative Concepts for Beneficial CO\textsubscript{2} Use, DOE indicated its intent to support “innovative concepts for beneficial CO\textsubscript{2} use, which include … mineralization to carbonates directly through conversion of CO\textsubscript{2} in flue gas … (into) chemicals.” Projects include “pilot-scale field testing of technologies for chemical conversion of CO\textsubscript{2} captured from industrial source, for permanent storage (e.g. mineralization) or processes that have a beneficial use of CO\textsubscript{2} that result in the production of fuels or chemical products.”

Although the chemical reactions for the mineralization of CO\textsubscript{2} are basic and very well known, additional assessment is needed to demonstrate how those basic chemical processes can be applied and scaled to reduce CO\textsubscript{2} emissions from large anthropogenic sources. There remain significant gaps in scientific and technical understanding of how to optimize the engineering design of a commercial-scale facility; how to respond to real-world factors, such as the quantity and quality of industrial emissions to maintain acceptable capture efficiencies and product quality; and how to access and deliver products to viable markets that will result in permanent storage of the CO\textsubscript{2} through end uses. The project must also ensure protection of human health and the environment, reduce costs, and facilitate the full-scale deployment of this technology. Comparing predictions from smaller-scale laboratory or pilots tests and numerical models with field results is necessary to validate the predicted benefits and demonstrate that scientific understanding is correct.

To address these experience gaps, the SkyMine\textsuperscript{®} pilot plant project has been designed to evaluate and successfully demonstrate:

- The feasibility of the capture and mineralization of CO\textsubscript{2} from a large, industrial emissions source on a pilot-scale that is readily and effectively transferable for commercial use;
- The commercial value and range of potential markets for the products produced from the mineralization of CO\textsubscript{2} from the process;
- The practicality of developing, constructing, and operating a commercially viable operation using existing labor and craft sources, materials, and infrastructure available in a typical urban or industrial area;
- The ability of the process to satisfy all necessary environmental permits, licenses, and other regulatory requirements and minimize the potential risks associated with construction and operation of this new technology; and
- The ability to complete the entire project on schedule and within budget.

3.5.3 Alternatives to Proposed Action

The DOE-provided opportunity, under this FOA, for a beneficial CO\textsubscript{2} use pilot project could be satisfied in several ways, one of which — the proposed action — is preferable. The proposed activity is set at an existing coal-fired, cement manufacturing plant where heavy industrial activity has occurred for several decades, where host plant operators are familiar to
the community and local conditions, where the centralized urban location provides ample access to infrastructure and product markets, and where the host plant and Skyonic Corporation have established strong collaborative agreements. The integration of the SkyMine® facility into an existing commercial operation will result in minimal impact to the environment and community, but will facilitate the efficient collection of large amounts of scientific data needed to assess the feasibility of the beneficial use of CO₂ through mineralization.

The proposed action is for the DOE to provide funding to the team led by the Skyonic Corporation to coordinate with Capitol Aggregates to capture approximately 75,000 metric tons per year (MTPY) of CO₂ from its flue gas stream and convert it into approximately 144,000 MTPY of sodium bicarbonate using the SkyMine® process.

3.5.3.1 “No Action” Alternative

“No action,” meaning that the proposed beneficial CO₂ use project is not implemented in any setting would delay planned development and deployment of larger-scale mineralization technologies for carbon capture by perhaps several years. The increased understanding of the factors that may influence the scaling of the technology to larger anthropogenic sources would not be gained, the development of new markets for the products of the mineralization process may not be realized, and no example of successful and safe CO₂ capture using mineralization, on any scale, could be offered to the public in support of a larger, more expensive project. The complexities of a larger pilot might translate to long delays in public and regulatory approval, thereby jeopardizing goals of rapid action on climate change issues.

3.5.3.2 Different SkyMine® Site Alternatives

Skyonic examined a number of coal-fired industrial sources located in three geographic regions of the United States. All of the sites were evaluated for technical and engineering suitability, which included characteristics such as access to flue gas, sufficient land 3-5 acres for the proposed plant site, adjacent rail-service, etc. Six sites located in the Midwest, Texas, and Southern California were identified as potential candidates and subjected to further consideration.

Skyonic entered into detailed negotiations with the operators at each of these sites to seek commitments to the SkyMine® pilot project. Of these operators, only the Zachry Corporation, owner of the Capitol Aggregates cement manufacturing plant in San Antonio, Texas, would provide a commitment for support, operational coordination, and corporate-level involvement necessary to make the project feasible in the timeframe set forth in the DOE Funding Opportunity Announcement.

3.5.3.3 Alternate SkyMine®/Carbon Capture Process Technologies
The proposal is intended to demonstrate the effectiveness of the SkyMine® technology to meet the DOE beneficial CO₂ use goal. Although the SkyMine® process is flexible and can be modified to produce various commercial products, the basic proposed technology has been well defined. No alternative technologies were considered.

3.5.4 EXISTING ENVIRONMENT

This section shall discuss the existing environment at the project location(s). The principal proposer and all proposed subcontractors shall discuss the following:

3.5.4.1 Land Use

The SkyMine® project site is on approximately 5 acres collocated at the 600-acre Capitol Aggregate cement manufacturing plant approximately 2.5 miles north of Interstate Highway 410, 2.0 miles west of Interstate Highway 35, 4.0 miles east of Texas Highway 281, and 3.3 miles south of Texas Highway 1604. The Capitol Aggregates property is bordered to the north by Thousand Oaks Drive, to the west by Wetmore Road, to the east by Nacodoches Road, and to the south by Wurzbach Parkway.

As shown on the 2001 USGS Land Use Survey map (Figure 3.16), a large portion of the area surrounding the Capitol Aggregates facility is highly urbanized with medium to high intensity commercial and residential development, major roadways, and small interspersed grassy greenbelts. The Capitol Aggregates site, including the proposed 5-acre SkyMine® project site, includes primarily barren land. The entire property has been developed for heavy industrial use since 1965.

A main line of the Union Pacific Railroad follows the western boundary of the Capitol Aggregates property and provides service to the site. A spur also branches just southwest of the property and follows the southern property line. Electrical power service is provided by the City Public Service (CPS) which serves the San Antonio metropolitan area and enters the site along a designated right-of-way from the southeast. No major pipelines are indicated on the topographic map to be in the proximity to the site.

The zoning for the SkyMine® project area and all of the surrounding Capitol Aggregates property is for industrial use. A small area of lots designated for single family residential use is approximately 1,000 feet to the east of the site, but the majority of the other adjacent property is zoned as either industrial or commercial. Figure 3.1.7 illustrates the zoning designations in the proximity of the proposed project site.
Figure 3.16
SkyMine® Project Area - 2001 USGS Land Use

NLCD 2001

Land Cover

- Open Water
- Perennial Ice/Snow
- Developed, Open Space
- Developed, Low Intensity
- Developed, Medium Intensity
- Developed, High Intensity
- Barren Land (Rock, Sand/Clay)
- Unconsolidated Shore
- Deciduous Forest
- Evergreen Forest
- Mixed Forest
- Dwarf Scrub (AK only)
- Shrub/Scrub
- Grasslands/Herbaceous
- Sedge/Herbaceous (AK only)
- Lichens (AK only)
- Moss (AK only)
- Pasture/Hay
- Cultivated Crops
- Woody Wetlands
- Emergent Herbaceous Wetlands
Figure 3.17
SkyMine" Project Area
Local Zoning Designations

11, 12 - Industrial
R6 - Single Family Residential
C3, C3 - Commercial
3.5.4.2 Atmospheric Conditions/Air Quality

The SkyMine® project area is located in San Antonio which is in the south-central portion of Texas on the Balcones Escarpment. Northwest of the city, the terrain slopes upward to the Edwards Plateau and to the southeast it slopes downward to the Gulf Coastal Plains. With its location on the northwestern edge of the Gulf Coastal Plain, San Antonio possesses a modified subtropical climate. Average monthly temperatures, in Fahrenheit degrees, range from the 50s in winter to 80s in summer. During winter the area is alternately influenced by a continental climate, when winds blow from the north and west and by a modified maritime climate, when south and southeast winds blow from the Gulf of Mexico. During the summer the climate becomes more tropical-like with prevailing south and southeast winds. The moderating effects of the Gulf of Mexico prevent extremely high temperatures; however, summers are usually long and hot with daily maximum temperatures above 90 over 80% of the time. San Antonio is situated between a semi-arid area to the west and a much –more moist and humid area to the east. Such a location allows for large variations in monthly and annual precipitation amounts. The normal annual precipitation for San Antonio is about 30 inches, although it may range from near 10 to near 50 inches from one year to another. The following Table 3.11 summarizes average climatic data for the National Climatic Data Center (NCDC, 2010).

Table 3.11
NOAA Southern Regional Climate Center
National Climatic Data Center (NCDC) Climate Normals
San Antonio, Texas

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg. Precipitation (inches)</td>
<td>1.71</td>
<td>1.81</td>
<td>1.52</td>
<td>2.50</td>
<td>4.22</td>
<td>3.81</td>
<td>2.16</td>
<td>2.54</td>
<td>3.41</td>
<td>3.17</td>
<td>2.62</td>
<td>1.51</td>
<td>30.9</td>
</tr>
<tr>
<td>Avg. Wind Speed (Dir./mph)</td>
<td>NE/10.4</td>
<td>NE/11.5</td>
<td>SE/11.5</td>
<td>SE/11.5</td>
<td>SE/11.5</td>
<td>SE/10.4</td>
<td>SE/10.4</td>
<td>SE/9.2</td>
<td>SE/10.4</td>
<td>S/10.4</td>
<td>NE/10.4</td>
<td>SE/10.8</td>
<td></td>
</tr>
<tr>
<td>Avg. High Temperature (Deg. F.)</td>
<td>60.8</td>
<td>65.7</td>
<td>73.5</td>
<td>80.3</td>
<td>85.3</td>
<td>91.8</td>
<td>95.0</td>
<td>95.3</td>
<td>89.3</td>
<td>81.7</td>
<td>71.9</td>
<td>63.5</td>
<td>79.5</td>
</tr>
<tr>
<td>Avg. Low Temperature (Deg. F.)</td>
<td>37.9</td>
<td>41.3</td>
<td>49.7</td>
<td>58.4</td>
<td>65.7</td>
<td>72.6</td>
<td>75.0</td>
<td>74.5</td>
<td>69.2</td>
<td>58.8</td>
<td>48.8</td>
<td>40.8</td>
<td>57.7</td>
</tr>
</tbody>
</table>

The SkyMine® project site is located in the San Antonio Metropolitan Statistical Area which is monitored by twelve air quality monitoring locations operated by the Texas Commission on Environmental Quality (TCEQ), as well as a number of local and private organizations. Table 3.12 includes information regarding the nearest air quality monitoring station to the SkyMine® project area (TCEQ, 2010a).
### Table 3.12
#### Air Quality Monitoring Stations

<table>
<thead>
<tr>
<th>Monitor Name</th>
<th>Location</th>
<th>Distance</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selma (C301)</td>
<td>Near I35</td>
<td>6.0 mile NE</td>
<td>PM2.5; PM10</td>
</tr>
<tr>
<td>San Antonio Scale (A140)</td>
<td>Near I35/I/10</td>
<td>7.5 miles S</td>
<td>Met Data only</td>
</tr>
<tr>
<td>San Antonio Downtown (C27)</td>
<td>Near I10</td>
<td>9.5 miles SSW</td>
<td>NOx; CO</td>
</tr>
<tr>
<td>Camp Bullis (C58)</td>
<td>Near I10/SH1604</td>
<td>10.5 miles NW</td>
<td>O3; NOx; Met Data</td>
</tr>
<tr>
<td>CPS Pecan Valley (C678)</td>
<td>Near I10/SH87</td>
<td>10.5 miles S</td>
<td>O3; Met Data</td>
</tr>
</tbody>
</table>

In April 2008, the entire metropolitan area, including Bexar County, was designated as attainment for the 8-hour National Ambient Air Quality Standard (NAAQS) for ozone (80 parts per billion (ppb)). The previous 1-hour ozone standard (120 ppb) was revoked in Bexar County in April 2009. The county is also in attainment of all other criteria pollutants identified in the Clean Air Act (CAA), including Sulfur Oxide (SOx), Particulate Matter (PM-10 & PM-2.5), Carbon Monoxide (CO), Nitrogen Dioxide (NOx), and Lead.

In 2008, the U.S. Environmental Protection Agency (EPA) tightened the 8-hour ozone standard to 75 ppb but has not yet formally designated any areas as nonattainment. In January 2010, EPA announced that it was reconsidering the revision of ozone standard and proposed a further tightening to between 60 – 70 parts per billion (ppb). Based on monitored ozone levels in the San Antonio area, it is highly likely that it will be designated as nonattainment and required to develop additional control strategies to reduce ozone (EPA, 2010a).

#### 3.5.4.3 Hydrologic Conditions/Water Quality

This section shall identify any watersheds and downstream drainage, surface and groundwater quality (nearby aquifers and the depth of groundwater) in the project area, existing floodplains, unique aquatic habitats, recreational areas, public water supplies; describe any constraints on water availability imposed by treaties, court decree, state and Federal water laws; and identify existing wastewater treatment and/or disposal facilities.

**Watershed:** The SkyMine® project area is in the San Antonio River Basin. A small, intermittent tributary (identify as Tributary F on some topographic maps) has been artificially diverted around the western boundary of the Capitol Aggregates property. Mud Creek is the closest perennial stream running north-south approximately 1.3 miles west of the project site. Beitel Creek also runs north-south approximately 2.0 miles east of the project site. All of these are tributaries to Salado Creek which runs west-east approximately 1.6 miles to the south of the project site (Figure 3.18) (TCEQ 2010b). Salado Creek is a tributary of the San Antonio River which ultimately flows to the Gulf of Mexico. Two small neighborhood lakes, Northern Hills Lake and El Dorado Lake are within 3 miles. The nearest large reservoir is Canyon Lake on the Guadalupe River approximately 23 miles north northeast of the proposed site.

**Surface Water Quality:** The TCEQ periodically monitors water quality in these streams and has detected impairments for aquatic life in the following segments (TCEQ, 2010c):

- Salado Creek (Segment ID 1910) – first listed in 2004. A review of the water quality standards for this creek is being conducted before a Total Maximum Daily Load (TMDL) plan is initiated.
• Upper San Antonio River (Segment ID 1911) from – first listed in 2006. Additional information is being collected before a TMDL plan is initiated. No other impairments have been noted in nearby monitored water bodies.

Wetlands: Several small, isolated wetlands have been identified in the U.S. Fish and Wildlife Service National Wetland Inventory (USFWS, 2010) in and around the SkyMine® project area, including riverine and palustrine wetlands. All of the wetlands located on the Capitol Aggregates property, with the exception of a small area of temporarily flooded riverine wetlands, are either excavated or diked impoundments. Some are permanently flooded while others are only temporarily or seasonally flooded. Figure 3.19 illustrates the locations and types of wetlands present.

Floodplains: The Federal Emergency Management Agency (FEMA) has surveyed the floodplains in the project area and developed detailed Flood Insurance Rate Maps (FEMA, 2010). While small areas identified as Special Flood Hazard Areas Inundated by 100-year Floods (Zones A) for the Salado Creek watershed occur on the Capitol Aggregates property, the proposed SkyMine® facility is located above the impacted area. Figure 3.20 shows the SkyMine® in relation to mapped flood hazard areas.

Aquatic Habitats: No unique aquatic habitats or recreational areas exist within the boundaries or in the proximity of the project area. The current and past industrial activity on the property has removed any aquatic habitats that may have once existed in the area.

Wastewater Treatment: Only three wastewater discharges are located in the proximity of the SkyMine® project area, two of which are the intermittent storm water discharges from Aggregates. Another discharge from a City Public Service facility is also located less than one mile south of the site on Salado Creek. The nearest San Antonio Water System facility discharge is over 6 miles to the south southwest on the San Antonio River.
Figure 3.18
SkyMine® Project Area – TCEQ Surface Water Body Viewer
<table>
<thead>
<tr>
<th>NWI Code</th>
<th>Class</th>
<th>Water Regime</th>
<th>Special Modifier</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Riverine</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R4SBAx</td>
<td>Intermittent Streambed</td>
<td>Temporarily Flooded</td>
<td>Excavated</td>
</tr>
<tr>
<td>R4SBA</td>
<td>Intermittent Streambed</td>
<td>Temporarily Flooded</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Palustrine</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PUSAx</td>
<td>Unconsolidated Shore</td>
<td>Temporarily Flooded</td>
<td>Excavated</td>
</tr>
<tr>
<td>PUBHx</td>
<td>Unconsolidated Bottom</td>
<td>Permanently Flooded</td>
<td>Excavated</td>
</tr>
<tr>
<td>PUSCh</td>
<td>Unconsolidated Shore</td>
<td>Seasonally Flooded</td>
<td>Diked Impoundment</td>
</tr>
<tr>
<td>PUBBHh</td>
<td>Unconsolidated Bottom</td>
<td>Permanently Flooded</td>
<td>Diked Impoundment</td>
</tr>
<tr>
<td>PSS1Ah</td>
<td>Scrub-Shrub Broadleaf Deciduous</td>
<td>Temporarily Flooded</td>
<td>Diked Impoundment</td>
</tr>
<tr>
<td>PUSCx</td>
<td>Unconsolidated Shore</td>
<td>Seasonally Flooded</td>
<td>Excavated</td>
</tr>
</tbody>
</table>
Figure 3.20
SkyMine® Project Area – San Antonio, Texas
FEMA Floodplain Maps

CITY OF SAN ANTONIO
480045

Approximate Location of Capitol
SkyMine® Project

ZONE X
**Groundwater:** Portions of two major aquifer systems, the downdip of the Trinity and the downdip of the Edwards Balcones Fault Zone (BFZ), are located in Bexar County and overlap at the project site. The regional geology is structurally complex due to deformation related to the Balcones fault zone, an intricate network of Miocene-age normal faults that trend northeast and are downthrown to the southeast (Clark 2009) (Figures 3.21 and 3.22).

The Edwards aquifer is a designated sole source aquifer and is the most prolific groundwater source in Bexar County. It provides water for agricultural, residential, commercial, and industrial purposes and supplies major springs that support recreational activities and businesses and offers habitat for several endangered species. The Trinity aquifer supplies water for residential, commercial, and industrial uses north of the San Antonio metropolitan area. The Glen Rose Limestone contains the upper Trinity aquifer and parts of the middle Trinity aquifer and it also forms the catchment area of the Edwards aquifer recharge zone to the south. The Glen Rose Limestone is relatively impermeable and is the primary lower confining unit of the Edwards aquifer (TWDB 2010).

Municipal, commercial, and industrial users extract water from the aquifer from 29 wells within approximately 2 miles. The depths of these wells range from 115 feet to 819 feet with most being over 400 feet. All of the wells in this area are into the Edwards downdip. The chemical quality of water in the aquifer is typically fresh, although hard, with dissolved-solids concentrations averaging less than 500 mg/l. The downdip interface between fresh and slightly saline water represents the extent of water containing less than 1,000 mg/l. Within a short distance downgradient of this “bad water line,” the groundwater becomes increasingly mineralized. Although the downdip of the Trinity Aquifer extends into Bexar County, it does not appear to be used as a significant source of groundwater in this area.

Since the Edwards Aquifer is a sole source aquifer and such an important economic and ecological resource in the area, regulatory programs have been put in place to protect both the quality and quantity of its water. Bexar County is regulated by the Edwards Aquifer Authority which was established by the Texas Legislature 1993 and began operations in 1996 (EAA 2010). A 17 member board of directors sets policy to manage, conserve, preserve, and protect the aquifer and works to increase recharge and prevent waste or pollution of the aquifer. The Edward Aquifer can be further divided into the Contributing, Recharge, and Artesian Zones (Figure 3.23). The SkyMine® project area falls within the Artesian Zone and although it may be subject to potential pumping restrictions or other requirements, no supplemental containment or runoff controls are required. Careful scrutiny of new construction activities for potential impacts on sensitive karst species is required and is discussed in more detail in Section 3.5.4.5.

The TCEQ also administers the Edwards Aquifer Protection Program (EAPP) established to enforce regulations on the construction and operation of facilities in the Contributing and Recharge Zones of the Edwards Aquifer (TCEQ 2010d). Figure 3.24 illustrates that the regulated Recharge Zone under the EAPP does not intrude into the project area, and more restrictive requirements on construction do not apply.
Figure 3.21
Edwards Balcones Fault Zone Aquifer Complex

Edwards (BFZ)
Figure 3.22
SkyMine® Project Area – San Antonio, Texas
Edwards (BFZ) and Trinity Aquifers

Figure 3.23
Edwards Aquifer Authority Zones
3.5.4.4 Geologic/Soil Conditions

Bexar County, in the interior belt of the Coastal Plain of South Central Texas, is crossed by the Balcones Escarpment, a geologic fault zone several miles wide consisting of several faults, most of which both dip and are downthrown to the east. It extends in a curved line across Texas from Del Rio to the Red River and is visible eastward from Del Rio, where it is about 1,000 feet high, and northeastward from San Antonio to Austin, where it is about 300 feet high. During the Miocene Epoch, as the ancestral Gulf of Mexico was subsiding to the southeast, the escarpment was created along a belt of weakness where episodic faulting occurred. In the roughly 20 million years since faulting ceased, the landscape had adjusted to this change in elevation between the older, harder limestone to the northwest and the younger, softer sediments and sedimentary rock to the southeast (White 2001).
The escarpment, which appears from the plains as a range of wooded hills, separates the west from the Coastal Plains. The Balcones zone was formed under conditions of strain during the Tertiary era, when a downwarping occurred near the Gulf Coast with a moderate uplift inland. The area northwest of the escarpment, about one-eighth of Bexar County, lies in high, hilly country, the source of numerous springs and artesian and underground wells. The altitude varies from 600 to 1,200 feet. In the far northwestern corner of the county are the Glenrose Hills, in which the highest elevations of the county are found. To the southeast lie the somewhat lower Edwards Flint Hills. The northern third of the county has undulating to hilly terrain, with alkaline soils over limestone and limy earths with shallow to deep loamy soils. The remainder of the county has very dark, loamy soils with some clayey subsoils and gray to black, cracking clayey soils with a high shrink-swell potential (TSHA 2010).

The SkyMine® project area lies in northeastern Bexar County in the transition area between the Edwards Plateau and the coastal plains. The elevation of the Capitol Aggregates facility ranges from 678 feet (above sea level) to approximately 840 feet. The project area is a previously cleared 4-acre portion of this property in the upper range of this elevation (780 – 840 feet).

Nine major soil types were identified in the Capitol Aggregates property by the National Cooperative Soil Survey by the Natural Resources Conservation Service (NRCS) of the U.S. Department of Agriculture (NRCS, 2010) (Figure 3.25). However, only one of these soil types, the Austin Silty Clay (AuC) is predominantly found on the portion of the property where the SkyMine® facility will be located. This soil type is characterized by a low, 3 – 5 inch well drained slope with no ponding or flooding potential.
### Bexar County, Texas (TX029)

<table>
<thead>
<tr>
<th>Map Unit Symbol</th>
<th>Map Unit Name</th>
<th>Acres in AOI</th>
<th>Percent of AOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuB</td>
<td>Austin silty clay, 1 to 3 percent slopes</td>
<td>81.4</td>
<td>18.2%</td>
</tr>
<tr>
<td>AuC</td>
<td>Austin silty clay, 3 to 5 percent slopes</td>
<td>98.0</td>
<td>22.0%</td>
</tr>
<tr>
<td>BrD</td>
<td>Brackett gravelly clay loam, 5 to 12 percent slopes</td>
<td>35.0</td>
<td>7.8%</td>
</tr>
<tr>
<td>BsC</td>
<td>Whitewright-Austin complex, 1 to 5 percent slopes</td>
<td>29.4</td>
<td>6.6%</td>
</tr>
<tr>
<td>HnB</td>
<td>Heiden clay, 1 to 3 percent slopes</td>
<td>28.2</td>
<td>6.3%</td>
</tr>
<tr>
<td>HsB</td>
<td>Houston Black clay, 1 to 3 percent slopes</td>
<td>43.5</td>
<td>9.8%</td>
</tr>
<tr>
<td>HuC</td>
<td>Houston Black gravelly clay, 3 to 5 percent slopes</td>
<td>63.3</td>
<td>14.2%</td>
</tr>
<tr>
<td>HuD</td>
<td>Houston Black gravelly clay, 5 to 8 percent slopes</td>
<td>44.0</td>
<td>9.9%</td>
</tr>
<tr>
<td>Tf</td>
<td>Tinn and Frio soils, 0 to 1 percent slopes, frequently flooded</td>
<td>23.3</td>
<td>5.2%</td>
</tr>
<tr>
<td><strong>Totals for Area of Interest</strong></td>
<td></td>
<td><strong>445.9</strong></td>
<td><strong>100.0%</strong></td>
</tr>
</tbody>
</table>

**Figure 3.25**

SkyMine® Project Area – NRCS Soil Types
3.5.4.5 Vegetation and Wildlife Conditions

The Texas Parks and Wildlife Department (TPWD) includes Bexar County in the far south-eastern extent of the Texas Blackland Prairie with the Edwards Plateau to the northwest, the Southern Texas Plains to the southwest, and East Central Texas Plains to the southeast. The Texas Blackland Prairie is a disjunctive ecological region distinguished from surrounding regions by its fine textured clayey soils and predominantly prairie potential natural vegetation. This region now contains a higher percent of cropland than adjacent regions, although much of the land has been recently converted to urban and industrial uses. Less than 5,000 acres of original prairie ecosystem remains statewide.

The SkyMine® project area is classified as an urban vegetative region (#46) (Figure 3.26) and little, if any, vegetation remains on the proposed site. Some small grassy patches and weeds are present, but do not represent significant habitat areas.
According to The Texas Parks and Wildlife Department 15 federally-listed endangered species, 6 state-listed (duplcative of federal listings), and 14 state-listed threatened species are known to occur in Bexar County. Over half of these species are arachnid, insect, and fish species that live only in karst features, springs, or other subterranean areas. Others are birds, mammals, or reptiles that generally live in relatively undisturbed or restricted habitats. Only two, the Western Burrowing Owl and the Interior Least Tern, are known to inhabit areas in or near man manmade structures or habitation. No known sightings of any of any endangered or threatened species have been reported at the proposed SkyMine® site, and occurrence is extremely unlikely due to the pre-existing disturbance by current and past industrial development and activity.
The TPWD Wildlife Diversity Program provided data from the Texas Natural Diversity Database (TXNDD) for the USGS topographic quadrangles in near the SkyMine® project site and identified the approximate locations of observed federal- and state-listed threatened, endangered, and rare species (TPWD, 2010c). The only sensitive species noted were two, federally-listed endangered, karst invertebrates, the Robber Baron Cave Meshweaver and the Cokendolpher Cave Harvestman, that live only in the Robber Baron Cave approximately 3 miles southwest of the site. The TPWD is careful to note that these data cannot provide definitive statement as to the presence, absence, or condition of special species, natural communities, or other significant features in any area. Nor can these data substitute for on-site evaluation by qualified biologists. However, further information from the U.S. Fish and Wildlife Service indicates that karst species are unlikely to occur on the SkyMine® project site.

The definitive report for FWS by George Veni entitled *Delineation of Hydrogeological Areas and Zones for the Management and Recovery of Endangered Karst Invertebrate Species in Bexar County, Texas*, (Veni 2003) delineates five zones that identify the probability of the presence of rare or endemic species. Those zones, slightly redefined here in recognition that the species are now listed, are:

**Zone 1**: Areas known to contain listed invertebrate karst species.

**Zone 2**: Areas having a high probability of containing suitable habitat for listed invertebrate karst species.

**Zone 3**: Areas that probably do not contain listed invertebrate karst species.

**Zone 4**: Areas which require further research but are generally equivalent to Zone 3, although they may include sections which could be classified as Zone 2 or Zone 5 as more information becomes available.

**Zone 5**: Areas which do not contain listed invertebrate karst species.

According to experts at the FWS, the SkyMine® project site is located in a Karst Zone 3 indicating that it probably does not contain listed invertebrate karst species.

The FWS also designates Critical Habitats for Threatened and Endangered Species and has identified several locations, primarily caves and other karst features, in Bexar County. The closest Critical Habitat is the Robber Barron Cave located approximately 3 miles southwest of the project site. Figure 3.27 illustrates the location of that Critical Habitat area in relation to the proposed project site.

Several, small, isolated wetlands have been identified in the U.S. Fish and Wildlife Service National Wetland Inventory on the Capitol Aggregates plant site near the proposed SkyMine® project area. All but one of these wetlands is excavated or impounded and most are only temporarily flooded. Small areas of floodplain also occur along and adjacent to the small, artificially-diverted, intermittent tributaries to Salado Creek near the project area. However, none of these wetlands, floodplains, or any other terrain represent sensitive habitats for endangered, threatened, or rare species.
Figure 3.27
SkyMine® Project Area – USFWS Proximity of Critical Habitats
3.5.5 ENVIRONMENTAL IMPACTS OF THE WORK TO BE PERFORMED

This section describes the anticipated environmental impacts from the project including all impacts and consequences of the project at the selected site.

3.5.5.1 Land Use

The construction and operation of the SkyMine® facility will be consistent with the existing heavy industrial land use conducted by Capitol Aggregates on the property since 1965. All activities occur on a <5 acre site to reduce the potential impact on the area and on existing operations of the approximately 600 acre cement plant site. Although the construction of various materials handling facilities, chemical processing units, storage tanks, rail spurs, and other support buildings will require typical excavation, leveling, and other site work necessary for proper foundation, piping, and containment structures, all activities will occur on previously disturbed and developed land.

The SkyMine® process is designed to recycle and reuse materials to the fullest extent possible. All of the chemicals used in the process will be converted into marketable products and shipped to customers via railcar or tanker truck. The only waste that is anticipated is activated carbon from the water purification process which may contain a very small amount of mercury and lead from the Capitol Aggregates emissions. The total quantity or frequency of waste generation has not yet been determined; however, the amount of mercury is expected to be less than 1.0 pounds per year and lead less than 1.6 pounds per year. Waste activated carbon filter materials containing these contaminants will be disposed of by a licensed waste management company.

Wastewater may also be generated during the brining process since sulfates must be removed from the brine before it is used in the production of sodium hydroxide. The total volume or quality of the effluent stream has not yet been determined, but it will be treated sufficiently to satisfy pretreatment discharge limits into the San Antonio Water System (SAWS). Skyonic is currently in discussions with SAWS to establish specific effluent criteria and limits. No surface impoundments are anticipated.

3.5.5.2 Air Quality Impacts

The SkyMine® will deliver approximately 300,000 tpy of the stack emissions from Capitol Aggregates coal-fired cement kiln and route it through an absorption tower to remove over 90 percent of its CO₂. As an additional benefit, this scrubbing process and the associated conditioning will also remove significant amounts of SO₂, NOₓ, and other regulated pollutants from the stack. The result will be a net decrease in emissions from the current Capitol Aggregates inventory. No other combustion source emissions, solvents, or chemicals are expected to be released from the process. Table 3.13 provides an estimate of the emission reductions anticipated from the Capitol Aggregates flue gas stream.

The two primary materials handling processes at the new SkyMine® facility will include salt unloading and transfers and bicarbonate production and handling. These will be controlled in accordance with accepted industry practices to minimize particulate emissions using closed conveyors or pneumatic systems with appropriate baghouse or
other filter devices. Heat will be used to dry the sodium bicarbonate during processing. In addition, a small amount of treated flue gas will be routed to the bicarbonate process. These processes will comply with the requirements of the TCEQ state permit-by-rule for minor sources that do not require individual permit authorizations. Similarly storage tanks and loading/unloading facilities for hydrochloric acid and sodium hydroxide will comply with TCEQ permit-by-rule requirements, as well. A small temporary boiler may be necessary to provide heat during the initial startup of the SkyMine® facility. This boiler will be used only for the startup process and will satisfy all conditions of the TCEQ permit-by-rule for minor sources. No federal New Source Review permits will be required. Final emissions are expected to be minimal and are estimated in Table 3.14.

### Table 3.13

**Estimated SkyMine® Process Emissions Reductions**

<table>
<thead>
<tr>
<th>Source</th>
<th>Max Hourly Emissions (lb/hr)</th>
<th>Max Annual Emissions (tons/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reductions of Flue Gas from CO₂ Scrubber</strong> (including flue gas conditioning)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOₓ – [5.09]</td>
<td>NOₓ – [22.30]</td>
<td></td>
</tr>
<tr>
<td>SO₂ – [31.22]</td>
<td>SO₂ – [136.74]</td>
<td></td>
</tr>
<tr>
<td>PM – [0.57]</td>
<td>PM – [2.53]</td>
<td></td>
</tr>
<tr>
<td>PM10 – [0.38]</td>
<td>PM10 – [1.64]</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄ – [0.22]</td>
<td>H₂SO₄ – [0.95]</td>
<td></td>
</tr>
<tr>
<td>Hg – [0.0001]</td>
<td>Hg – [0.0005]</td>
<td></td>
</tr>
<tr>
<td>Pb – [0.0002]</td>
<td>Pb – [0.0008]</td>
<td></td>
</tr>
<tr>
<td>HCl – [0.0148]</td>
<td>HCl – [0.0200]</td>
<td></td>
</tr>
</tbody>
</table>

[Bracketed] values indicate reductions of compounds previously emitted from Capitol Aggregates stack.

All values reported to the nearest 0.01 (except Hg, Pb & HCl to nearest 0.0001)

### Table 3.14

**Estimated SkyMine® Process Emissions**

<table>
<thead>
<tr>
<th>Source</th>
<th>Max Hourly Emissions (lb/hr)</th>
<th>Max Annual Emissions (tons/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Operations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ – 3136.97</td>
<td>CO₂ – 1252.45</td>
<td></td>
</tr>
<tr>
<td>NOₓ – 1.40</td>
<td>NOₓ – 2.37</td>
<td></td>
</tr>
<tr>
<td>SO₂ – 0.04</td>
<td>SO₂ – 0</td>
<td></td>
</tr>
<tr>
<td>CO – 2.77</td>
<td>CO – 8.24</td>
<td></td>
</tr>
<tr>
<td>PM – 4.36</td>
<td>PM – 19.07</td>
<td></td>
</tr>
<tr>
<td>PM10 – 0.25</td>
<td>PM10 – 0</td>
<td></td>
</tr>
<tr>
<td>Hg – 0</td>
<td>Hg – 0</td>
<td></td>
</tr>
<tr>
<td>Pb – 0</td>
<td>Pb – 0</td>
<td></td>
</tr>
<tr>
<td>VOC – 0.10</td>
<td>VOC – 0</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄ – 0</td>
<td>H₂SO₄ – 0</td>
<td></td>
</tr>
<tr>
<td>HCl – 0.0192</td>
<td>HCl – 0.0803</td>
<td></td>
</tr>
<tr>
<td>Cl – 0.0010</td>
<td>Cl – 0.0043</td>
<td></td>
</tr>
</tbody>
</table>

All values estimated to the nearest 0.01 (except Hg, Pb, Cl, & HCl to nearest 0.0001)

Emissions from construction operations are expected to be typical of those for any heavy industrial project, including the operation of bulldozers, graders, backhoes, concrete trucks, and other heavy non-road construction equipment for land clearing, leveling, and foundation preparation. Site preparation is expected to take approximately 17 weeks.
Building, tank, and structural construction will require cranes, generators, and other equipment for fabrication and assembly and is expected to take an additional 18 weeks. Process equipment installation and remaining work will occur concurrently but will extend an additional 17 weeks. Table 3.15 provides an estimate of the type and number of pieces of heavy diesel construction equipment that may be required on-site. All appropriate dust suppression and emission control practices will be followed to minimize short-term impacts from these activities. Emissions from construction will be temporary and typical for this moderate industrial construction project.

<table>
<thead>
<tr>
<th>Activity</th>
<th>Equipment Used</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site Preparation &amp; Foundation</td>
<td>3 bulldozers</td>
<td>3 months</td>
</tr>
<tr>
<td>Underground Piping</td>
<td>1 bulldozer; 2-3 backhoes</td>
<td>3 months</td>
</tr>
<tr>
<td>Process Equipment &amp; Pipe Bridging</td>
<td>3-4 medium cranes</td>
<td>6 months</td>
</tr>
<tr>
<td>Scrubber Tower Installation</td>
<td>1 heavy lift crane</td>
<td>few days</td>
</tr>
<tr>
<td>Overhead Work &amp; Miscellaneous</td>
<td>Manlifts, light equipment</td>
<td>6 months</td>
</tr>
</tbody>
</table>

### 3.5.5.3 Hydrological Conditions/Water Quality

The SkyMine® operations will have no direct discharges to adjacent water bodies and will not require an individual National Pollutant Discharge Elimination System (NPDES) permit. Any process wastewater that may result from brining or other activities at the SkyMine® plant will be treated to satisfy pretreatment requirements and discharged into the SAWS collection system. An estimated average effluent flow of 100 gallons/minute may result from process discharges. Discharges will be permitted by SAWS and monitored to ensure compliance with all water quality discharge criteria.

Construction activities will comply with the requirements of the TCEQ General Permit (TXR 150000) for storm water from a small construction activity affecting more than one but less than five acres. In accordance with that General Permit, Skyonic will prepare and implement a Storm Water Pollution Prevention Plan (SWPPP), post a notice at the site, and submit a site notice to the affected Municipal Sanitary Storm Sewer System (MS4) operator (San Antonio Water System). Skyonic and its contractors will apply construction best management practices in order to minimize the discharge of pollutants in storm water runoff. Since the SkyMine® project area is wholly contained within the Capitol Aggregates property, all storm water runoff will flow into the Capitol Aggregates retention ponds and be recycled. Additional efforts will be required to ensure that no contamination is released that would adversely impact the Capitol Aggregates operations, providing an additional measure of control of runoff from the SkyMine® plant site.

Upon completion of the construction activities, the operation of the SkyMine® facility will be covered by the TCEQ Multi-Sector General Permit (TXR050000) for on-going
industrial activities. This general permit also requires Skyonic to prepare, implement, and maintain a SWPPP to reduce or prevent contaminants from affecting nearby water bodies. Most of the processes and operations at the facility will be totally enclosed and not subject to runoff. Other areas will be monitored and controlled not only to satisfy the regulatory requirements, but to avoid potential interference with Capitol Aggregates operations, as well.

In the highly unlikely event of a significant spill at the SkyMine® plant, potential contamination of groundwater will be prevented by the construction and maintenance of containment systems around all storage tanks and process areas, as well as by automated shutoff systems to restrict and neutralize any accidental release of chemicals. Although such leaks are most likely to occur from the hydrochloric acid and sodium hydroxide storage tanks, sufficient types and quantities of chemicals are used in the SkyMine® process to quickly and effectively neutralize any potential spills that may occur. The highly alkaline soils and subsurface limestone in the area, as well as over 300 feet of overburden, would further serve to neutralize or buffer any spills before it could contaminate groundwater.

The SkyMine® process will capture 8.5 million gallons/year of the water directly from the moisture in the stack emissions from Capitol Aggregates using heat exchangers. Several options are available for obtaining additional process water. Water can be purchased from SAWS which has several large water supply mains readily available in the area that have sufficient capacity to accommodate this demand. SAWS’ officials have confirmed that connections to the municipal water system can be made without any significant impact on water supplies in the area.

SAWS also operates the largest recycle water system in the county providing high quality, treated effluent for non-potable water uses to a large part of the San Antonio area. SAWS guarantees an uninterrupted supply of recycled water to participating users that cannot be curtailed, even during times of severe drought. Unfortunately, while this water may be of sufficient quality to meet process needs, no recycled water mains are currently located near the proposed SkyMine® project site. Extending the system to the site is possible but may be cost prohibitive. Expansions of the system could make recycled water available in the future.

Capitol Aggregates uses water from three on-site groundwater wells and two surface water ponds and can produce more than it currently needs for its own processes. It also has a significant allocation from the Edwards Aquifer Authority that exceeds its own current demands and has indicated that it may be able to provide water for all or part of the SkyMine® project’s needs.

3.5.5.4 Geologic/Soil Conditions

This section shall describe any subsidence that might be caused by construction; any possible erosion, stream diversion, floodplain and wetland intrusion, and any increases or decreases in soil permeability and filtration.
Although Bexar County lies along the Balcones Fault, no movement has occurred for over 20 million years. The limestone geology of the area is extremely stable and extensive urbanized areas have developed throughout the area. All of the small tributaries to Salado Creek have either been diverted around the Capitol Aggregates quarry and cement plant or will not be affected by the infrequent, intermittent runoff that may result from seasonal rainfall. The addition of the SkyMine® facility at the site will not significantly alter the established drainage pattern or quantity of flow. Although small areas of floodplain exist in lower section of the Capitol Aggregates property near the three retention ponds, and several isolated, seasonal or impounded wetlands are located on the property, none exist in the 4 acres proposed for the SkyMine® project. The predominant soil type on the site, Austin silty clay, is well drained with a very shallow slope. Since the site has already undergone significant disruption from previous industrial activity, the construction of the proposed units will not significantly impact soil permeability or filtration characteristics of the area.

3.5.5.5 Vegetation and Wildlife Resources

The proposed SkyMine® project area has undergone significant disruption from previous industrial activity and has little or no remaining habitat suitable for sensitive species. The entire area is barren land being used for storage of large metal parts and equipment. Heavy industrial activity from the cement plant and the quarry and associated truck and vehicle traffic continually disturb the site making current or future habitation very unlikely.

The nearest location of listed species, the Robber Baron Cave Meshweaver and the Cokendolpher Cave Harvestman, endangered karst invertebrates inhabiting an isolated cave, is approximately 3 miles away. The U.S. FWS has characterized the area as a Karst Zone 3 with a low probability of the occurrence of any sensitive species. The floodplains and wetlands near the site on the Capitol Aggregates property have also been significantly modified or are artificial impoundments which are not ecologically sensitive or sustainable, even without the addition of the SkyMine® facility. No impacts to any of these features are anticipated from the proposed project.

3.6 CO₂ LIFECYCLE

Skyonic completed a lifecycle analysis of the total carbon footprint benefit of capturing CO₂ using and input/output model of the SkyMine® project designed under the Phase 1 grant. This lifecycle model extends carbon-effect modeling to all inputs and outputs of the process (including feedstock, water, electricity, and produced products) and is supported by the EPC-generated plant scale process flow model.

3.6.1 Elements of Lifecycle

In order to accomplish the Lifecycle Analysis task in a manner consistent with DOE/NETL practices, the following elements are included in this study:
i. A high-level Process Flow Diagram with a generalized mass balance of the plant is found at Figure 3.28. This diagram defines the masses of the major process inputs and outputs of the SkyMine® Pilot Plant sufficient to conduct a Lifecycle Analysis in a manner consistent with prior practice as outlined by DOE documents and guidelines to include the identification of individual process streams that are traceable throughout the subsequent calculation of carbon effects. This mass balance was prepared by the qualified EPC subcontractor, Ford, Bacon & Davis, and is offered as the most accurate representation of the plant inputs and outputs as estimated by best practices engineering methods and backed by state-of-the-art simulations.

ii. Generalized Energy Budget of the plant (Table 3.16). This chart defines the gross maximum possible, full draw electrical load on all units of the plant. This energy balance was prepared by Ford, Bacon & Davis and is the most accurate representation of the plant inputs and outputs as estimated by best practices engineering methods and backed by state-of-the-art simulations.

---

**Figure 3.28 — Primary Inputs and Outputs of SkyMine® Project with Primary Mass-balance Terms (Numbers in Figure 3.28 refer to Table 3.17)**
a. Valid Life Cycle Analysis is not based upon the gross maximum possible full draw electrical load on devices (though such information is required for appropriate sizing of the transformer/rectifier, and safety margins on plant equipment). Valid Lifecycle Analysis requires the calculation of average annual energy consumption, and a comparison of same to average annual carbon capture.

b. The SkyMine® Pilot Plant engages in various activities related to its commercial operations on site, and its utility as an operating plant, both of value to the host site (Capitol Aggregates Cement Plant) and to the SkyMine® private sector investors. Both parties expect these non-carbon-capture functions to be performed. These non-carbon-capture activities include the production of chemical byproducts (for the benefit of private sector investors) and non-carbon scrubbing of Capitol Aggregates flue gas (for the benefit of the host, Capitol Aggregates). Valid Lifecycle carbon analysis must account for only the energies consumed in capturing carbon dioxide. Therefore, the energies consumed in these host and investor-serving activities are excluded from the Lifecycle Analysis basis; e.g. in a “pure carbon capture, only,” facility, these byproduct energy expenses could be minimized or dispensed with entirely.

c. The gross energy budget prepared by Ford, Bacon & Davis includes some engineering estimates of operation which conform to traditional, conservative estimation and necessary guard banding. Skyonic Corporation, its investors, and DOE/NELC are not engaging in this project for the purpose of determining how best to guard band traditional plant construction, but to assess how well a pilot scale plant can be operated to best capture carbon, while utilizing commercially available off-the-shelf equipment, and by operating said equipment in the process corner and regime that achieves the maximum carbon reduction at the least net energy to the national energy system. To that end, Skyonic Corporation will operate to expected, not guard banded, energy values.

iii. Skyonic Corporation will operate the chlor-alkali electrolyzers of the plant at a somewhat higher pressure than is traditional; though in a regime that has been characterized by the qualified electrolyzer manufacturer. This higher pressure regime has the effect of reducing the volume of bubbles of evolved gases formed in the reaction (hydrogen in the catholyte, chlorine in the anolyte), and this reduces the bulk resistance of these fluids to the passage of DC electricity, thus lowering the total resistance of the electrochemical circuit, and reducing the power necessary to manufacture a given amount of hydrogen/chlorine caustic. Skyonic Corporation will operate the chlor-alkali electrolyzers of the plant at an operating point characterized by optimization for lowest energy production of caustic; this is unlike a traditional chlor-alkali operation which is normally bound by a requirement to produce high concentration caustic soda. In traditional chlor-alkali operations, where caustic soda is produced as an end product, the intermediate production of high concentration caustic liquor is desirable as the need to further use energy intensive evaporators to produce further concentrated caustic or dry pellet caustic is benefited by the feed of strong liquor caustic from the cells. SkyMine® carbon capture requires no such high concentration of caustic, and can therefore be optimized to a lower kWh/tonne caustic production, and the evaporation steps of normal caustic post treatment are wholly dispensed with in the SkyMine® process.
iv. Skyonic Corporation has available on-site at SkyMine® relatively large quantities of waste heats from the cement plant host. The direct heat transfer of these low-grade heats are sufficient to heat electrolytic fluids to temperatures that are as high as can be borne by current membranes; this heat transfer allows high-temperature cell operation even at low currents and low voltages, where traditional chlor-alkali operation would fail to “self-heat” sufficiently to maintain operation. Skyonic Corporation will operate the SkyMine® pilot plant to optimize this use of waste heat, and estimates that at least 3% of total input power can be potentially reduced by these means alone.
All of the above effects result in the following Energy Budget for the SkyMine® project:

<table>
<thead>
<tr>
<th></th>
<th>Adjust of expected vs. guaranteed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolysis</td>
<td>14.67</td>
</tr>
<tr>
<td>Balance of Plant</td>
<td>0.07</td>
</tr>
<tr>
<td>Total</td>
<td>14.74</td>
</tr>
<tr>
<td>Carbon Capture MW</td>
<td>14.25</td>
</tr>
</tbody>
</table>

Table 3.16 — Energy Budget for SkyMine®

This calculation of energy spent in carbon-capture shows that the input energy figure presented in the Phase 1 application (14.25 MW) will be attained by Skyonic Corporation through a process engineering reduction 3% below the EPC-generated power consumption plan.

With the main power draw of the carbon capture processes established above (14.25 MW), a valid Lifecycle Analysis must include measuring direct effects of the SkyMine® process on the surrounding environment. Each process and sub-process must be compared to currently competing processes present in the marketplace (which would be displaced by chemicals sold by the SkyMine® facility) to ascertain comparable or lower impact. This analysis examines not only the CO₂ directly associated with the capture system and supporting chemical processes, but also includes CO₂ associated with production and transport of feedstock to the facility, products transported from the facility, and energy inputs to the facility, as depicted in Figure 3.28.

The raw materials utilized in the SkyMine® process are salt, flue gas, and water. Produced products include sodium bicarbonate (baking soda), hydrochloric acid, and bleach, and result in small amounts of liquid and solid wastes. The CO₂ generated by production and transportation of input feedstock and energy, and delivery of output commodity chemicals to customers is tabulated as a differential versus traditional approaches of producing the commodity chemicals.

Figure 3.28 provides a block diagram of the sources of the proposed SkyMine® project. The basic approach of this life cycle analysis is to combine the CO₂ capture within the SkyMine® facility with the CO₂ footprint of each of the inputs and outputs to and from the facility. Where commercial commodities are produced by the SkyMine® process, the CO₂ footprint of conventional approaches to making those commodities is estimated and deducted from the parallel activity for SkyMine®.

The various activities of the SkyMine® process, which correspond to the items identified in Figure 3.28, are identified below in Table 3.17 for easy reference.
<table>
<thead>
<tr>
<th>ID</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Extraction of salt (NaCl) from sea water through solar evaporation</td>
</tr>
<tr>
<td>2</td>
<td>Transport of the salt to the site, by barge to port</td>
</tr>
<tr>
<td>3</td>
<td>Transport by train to San Antonio</td>
</tr>
<tr>
<td>4</td>
<td>Provide the necessary water to sustain the process, i.e. makeup water</td>
</tr>
<tr>
<td>5,7</td>
<td>Chlor-alkali process energy 14.25 MW as calculated above</td>
</tr>
<tr>
<td>6</td>
<td>Flue gas enters the process and after being cooled from an initial temperature of approximately 125°C to 35°C through two heat exchangers, enters a knockout condenser where SO_x, NO_x, Hg, other heavy metals and water are removed. Energy included in balance-of-plant estimate above.</td>
</tr>
<tr>
<td>8</td>
<td>Capture of carbon dioxide from conditioned flue gas emissions by reaction with aqueous sodium hydroxide to form sodium bicarbonate.</td>
</tr>
<tr>
<td>9</td>
<td>Combustion of hydrogen and chlorine to form hydrochloric acid in the presence of a small amount of excess hydrogen. (Zero energy input: Spontaneous reaction)</td>
</tr>
<tr>
<td>10</td>
<td>The remaining chlorine is reacted with sodium hydroxide to form bleach (sodium hypochlorite). (Zero energy input: Spontaneous reaction)</td>
</tr>
<tr>
<td>11</td>
<td>Dry the sodium bicarbonate. Energy included in balance-of-plant estimate above.</td>
</tr>
<tr>
<td>12,13</td>
<td>Sell the hydrochloric acid, sodium hydroxide and bleach for industrial use. Transport the respective chemicals to market.</td>
</tr>
</tbody>
</table>

Table 3.17 - Process Steps (depicted in Figure 3.28)

3.6.2 Inputs/Outputs (See process activities in Table 3.17 and Figure 3.28)

The remainder of this section presents eight (8) activities for which the flow of materials and energy into and out of the proposed SkyMine® facility are evaluated and compared to analogous flows for conventional commercial processes that produce similar commodities. The net CO_2 generation for the mining and transport of raw materials was calculated using available data from established sources. These values are comparable to the industry standard, so they are a net neutral for the SkyMine® process versus a competing process, e.g. standard chlor-alkali. These figures are calculated to provide a sense of their contribution relative to the total energy requirements of the main process.
**Activity 1: Solar Evaporation ponds for salt, 4500 tonnes every two weeks.**

![Figure 3.29 – Solar Evaporation Pond](image)

Using data obtained from the salt works operation, electricity consumption is represented in Table 3.18.

<table>
<thead>
<tr>
<th><strong>Monthly Electricity Consumed in the Plant</strong></th>
<th>Total kw/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOTAL Year</td>
<td>1,318,197</td>
</tr>
<tr>
<td>NET TOTAL</td>
<td>599,869</td>
</tr>
<tr>
<td>Kw/h/TON washed net</td>
<td>2.20</td>
</tr>
<tr>
<td>Kw/h per 120000 TONS</td>
<td>263,697</td>
</tr>
</tbody>
</table>

**Table 3.18 – Electricity Consumption of Salt Plant**

The corresponding calculations are as follows:

\[
\text{Power consumption} = 2.2 \text{ kwh/ton} \times 124,956 \text{ MTPY} \times (1/8760 \text{ hr/yr}) = 31 \text{ kW}
\]
CO₂ generation: Assume pumps and conveyor belts are diesel powered. 0.0776 kg CO₂/MJ based on a CO₂ emission factor of 3.0 kg/L and a diesel heating value of 38.7 MJ/L.¹ Basis 1 year.

\[
31 \text{ kW} = 0.031 \text{ MW};\ 0.031 \text{ MW} \times 0.0776 \text{ kg CO}_2/\text{MJ} = 0.00241056 \text{ kg CO}_2/\text{sec} \\
0.00241056 \text{ kg CO}_2/\text{sec} \times 3600 \text{ sec/hr} \times 24 \text{ hr/day} \times 365 \text{ days/yr} = 76019 \text{ kg/yr} \approx 76 \text{ MT/year}.
\]

**Activity 2: Ship salt by Barge to port, 690 miles / 1110 km.**

The emission factor of fuel combustion for barge (heavy fuel oil) is 81,695 g CO₂/MMBTU.² The energy used in freight transportation for ships is 411 BTU/ton-mile.³

To get the energy requirement for shipping per year: 411 BTU/ton-mile * 1.103 ton/tonne * 4500 tonnes * 690 miles * 26 excursions/year = 3.66 * 10¹⁰ BTU's = 36,597 MMBTU's; 36,597 MMBTU's * 81,695 g CO₂/MMBTU's * (1/1000000 tonnes/gm) = 2,990 tonnes CO₂/year

**Activity 3: Ship by train from port to San Antonio: 4,500 metric tons every 2 weeks, 366 miles/588km.**

The emission value for freight trains of 404 ton-miles/gallon fuel was obtained from the website of the Federal Railroad Administration.⁴ Multiplying this value by the average weight and distance using some conversion factors gives the fuel usage per trip. The amount of CO₂ generated per excursion can be found by multiplying the fuel usage times the rate of 10.1 kg CO₂ per gallon of fuel published by the EPA⁵

\[
\text{Transport by train (366 miles} \times 4500 \text{ tonnes/2wks} \times 1.103 \text{ tons/tonne) / 404 ton*miles/gallon = 4496 gallons / 2wks} = 116912 \text{ gallons /yr}; \\
116912 \text{ gallons /yr} \times 10.1 \text{ kg /gallon} \times 1/1000 \text{ tonne/kg} = 1180.8 \text{ tonnes CO}_2 /\text{yr}.
\]

Therefore, the transportation total is approximately 4300 M Tonne CO₂/yr as represented below in Table 3.19.

---


⁵ From the EPA website [http://www.epa.gov/otaq/climate/420f05001.htm](http://www.epa.gov/otaq/climate/420f05001.htm)
### Table 3.19 Transportation Total

<table>
<thead>
<tr>
<th>Activity</th>
<th>Transportation Total (M Tonne CO$_2$/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt Preparation</td>
<td>76</td>
</tr>
<tr>
<td>Barge Transport</td>
<td>2990</td>
</tr>
<tr>
<td>Train Transport</td>
<td>1181</td>
</tr>
<tr>
<td>Total</td>
<td>4247</td>
</tr>
</tbody>
</table>

**Activity 4: CO$_2$ associated with obtaining Process Water**

Given the previous calculation of process makeup water as 208,400 tonnes/yr The energy requirements can be calculated with the following value:

$$
1939 \text{ kwh/Million Gallons}^6; 208,400 \text{ MT} / \text{yr} \times (\text{yr}/8760 \text{ hr}) \times (2205 \text{ lb/MT} \times 10^{-6} = 12.2 \text{ kw} ; \text{CO}_2 \text{ generation can be estimated by using the value of 1100 lb/MWh}^7 \text{ for CO}_2 \text{ generated per unit of power:Energy use/t} = 1100 \text{ lb/MW-hr} \times 1 \text{ tonne/2205 lb} \times (1 \text{ MW/1000 kw}) = 4.989 \times 10^{-4} \text{ tonne/kw-hr} = 2004 \text{ kw-hr/tonne CO}_2 \text{ generation/yr (makeup water)} = (12.2 \text{ kw})(1/2004 \text{ tonne/kwhr}) \times 8760 \text{ hr/yr} = 53.3 \text{ tonnes CO}_2/\text{yr}.
$$

**Activities 5, 7: Chlor-Alkali processing energy** (calculated above in Electrolysis from EPC design – See Table 3.16)

**Activities 6, 8: Flue gas processing** (included in Balance of Plant estimate from EPC design – See Table 3.16)

**Activities 9, 10: Hydrogen/Chlorine Combustion** and bleach formation are spontaneous self-driven reactions. All parasitic energies are included in gross EPC plant design estimate.

---


7 Obtain form CPS power in San Antonio, TX from the link http://www.cpsenergy.com/files/Historical_CO2_Intensity.pdf
Activities 11, 12: Drying bicarbonate, loading acids and solids to rail energies contained in gross plant budget.

Activity 13: Transport of product to market

As with input raw materials, the transport of output raw materials is expected to have the same CO₂ footprint for the Skyonic project as for conventional manufacturing approaches. Hence, in general, the net additional contribution of CO₂ from shipping products to market, compared to conventional sources, will be zero. The calculations which follow are intended to provide a reasonable estimate of the footprint of each sub-process, not counting alternative source footprints, but the figures are netted to zero in the summary data presentation in Tables 3.21 and 3.22. The marketplace is the greater Houston area: Distance from San Antonio is approximately 200 miles.

<table>
<thead>
<tr>
<th>Product</th>
<th>Annual Volume tonnes/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bleach NaOCl</td>
<td>52,847</td>
</tr>
<tr>
<td>Hydrochloric Acid HCl</td>
<td>184,316</td>
</tr>
<tr>
<td>Sodium Bicarbonate NaHCO₃</td>
<td>149,664</td>
</tr>
</tbody>
</table>

Table 3.20 - Product Volume

3.6.3 CO₂ Emissions

CO₂ emissions - NaOCl (bleach): Due to high chemical reactivity bleach must be transported via truck to its most immediate destination. CO₂ emission for heavy duty diesel truck is 79,616 g CO₂/MMBTUs fuel input

Energy used in transportation of freight for trucks: 2,800 BTUs/ton-mile. Trucks carry 20 tonnes per excursion. Calculate number of excursions: 52,847 MTPY ÷ 20 tonnes = ~2642 deliveries; Calculate BTUs/year for all deliveries: 2800 BTU/ton-mile * 20 tonnes/truck * 1.103 ton/tone * 200 miles * 2643 deliveries ÷ 10^6 =32,650 MMBTU/year; 32,650 MMBTU/year * 79,616 g CO₂/MMBTU ÷ 10^6 g/tonne = 2600 MTPY CO₂ (transport of bleach)

CO₂ emissions - HCl: Use the train 90 tonnes per car and 50 cars per excursion (4500 tonnes per excursion): Calculate number of excursions: 184,316 tonnes/4500 tonnes = 41

---

8 GREET 1.5 – Transportation Fuel-Cycle Model, Volume 2: Applications of Data and Results, Argonne National Lab Report.
excursions/year; (200 miles * 4500 tonnes * 1.103 tons/tone * 41 excursions) ÷ 404 ton-miles/gallon= 100,074 gallons/yr; 100,074 gallons/yr * 10.1 kg/gallon ÷ 1000 g/tonne = 1018 MTPY

CO₂ emissions - NaHCO₃: Calculate number of excursions: 149,664 tonnes/4500 tonnes = ~34 excursions/year; (200 miles * 4500 tonnes * 1.103 tons/tone * 34 excursions) ÷ 404 ton-miles/gallon= 83544 gallons/yr; 83544 gallons/yr * 10.1 kg/gallon ÷ 1000 g/tonne = 843.8 MTPY; Total CO₂/year from transport of products: 1018 + 843.8 + 2600 = 4461.8 MTPY = approximately 4500 MTPY

3.6.4 Energies and Carbon Calculations for Displaced Products

3.6.4.1 Energy Requirements for Electrolytic Products

Discussion of HCl and bleach production: The two reactions to produce these final products from intermediate products are both spontaneous and exothermic:

ΔG  ΔH

\( \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Cl}_2 = \text{HCl(aq)} \) 
-131.08 kJ/mol 
-166.7 kJ/mol

\( \text{Cl}_2 + 2\text{NaOH(aq)} = \text{NaCl(aq)} + \text{NaOCl(aq)} + \text{H}_2\text{O} \) ***highly exothermic and spontaneous

Virtually all of the energy needed to produce both of these chemicals is due to the manufacture of precursor chemicals, i.e. NaOH, Cl₂ and H₂, which are produced in the chlor-alkali reaction. The only energy cost associated with this specific reaction is the energy required for pumping the reactants to the reactor vessel, and operating the heat exchanger to carry off excess heat. Thus the SkyMine® chlor-alkali process will be compared to the chlor-alkali industry standard.

Chlor-Alkali Industry Standard: Calculate Energy (US Avg.) year 2006¹¹; year 2006¹²

---

¹⁰ Sodium Hypochlorite Production processes – Solvay Chlorinated Inorganics, obtained from the link

¹¹ Chlorine: History, Manufacture, Properties, Hazards, and Uses pp. 7-13, Obtained from the link

¹² World Chlorine Council,
% Mercury 6% x 3560 kwh/M tonne Cl₂ = 213.6 kwh/M tonne Cl₂

% Diaphragm 66% x 3580 kwh/M tonne Cl₂ = 2362.8 kwh/M tonne Cl₂

% Membrane 23% x 2970 kwh/M tonne Cl₂ = 641.7 kwh/M tonne Cl₂

Average energy consumption per tonne chlorine 3218.1 kwh/tonne Cl₂ (US Avg.)

Skyonic uses the metric “kwh/M tonne CO₂” (M tonne = metric tonne) since the process is based on CO₂ capture. The energy requirements of conventional chlor-alkali (above) can be converted from kwh/tonne Cl₂ to kwh/M tonne CO₂ using the following calculations:

Since the reactions are:

NaCl(aq) + H₂O = \( \frac{1}{2} \) H₂ + \( \frac{1}{2} \) Cl₂ + NaOH(aq)

NaOH(aq) + CO₂ = NaHCO₃(aq)

The ratio of moles Cl₂ to CO₂ is 1:2, and the molecular weight of Cl₂ is 70.9 and for CO₂ the value is 44.01.\[ \frac{(70.9 \text{ gm/mole Cl}_2)}{(44.01 \text{ gm/mole CO}_2)} \times \frac{(0.5 \text{ mole Cl}_2)}{\text{mole CO}_2} \]

\[ = 0.7964 \text{ wt.Cl}_2 / \text{wt. CO}_2 \]

3218.1 kwh/M ton Cl₂ * 0.7964 M ton Cl₂/M ton CO₂ = 2562 kwh/ton CO₂ (US avg). Combining this calculated US average energy consumption for traditional chlor-alkali with the amount of CO₂ captured per the Skyonic process yields an electricity “credit” for the Skyonic process as follows:

76,488 tonne/yr. * 2562 kwh/tonne * (yr/8760 hr) (0.001MW/kw) = 22.42MW (US Avg.)

However, the actual chlor-alkali cell, which includes bleach production, runs at 14.25 MW.

Therefore the comparison of the SkyMine® energy usage with the US average in energy in consumption is 14.25MW / 22.42 MW = 64% or 36% lower.

Reduction of CO₂ generation: The following calculations assume that power is produced by a natural gas combined cycle power plant, with a CO₂ emission rate of 936 #CO₂/MWh, or 2350 kwh/tonne CO₂.(22.42 MW * 8,760,000 hr/yr*(kw/MW) ÷ 2350 kwh/M tonne = 83,459 tonnes/yr less CO₂.

Calculating the energy savings using 45% average natural gas turbine efficiency and a heating value of 13,371 kWh/MTonne is thus: 8694 MTONnes/yr * 14,842 kWh/MTonne * 45% * (1/8,760,000) = 6.6 MW. And a CO₂ reduction of: 6.6MW * 1 MTONne CO₂/2.3530 MWh x 8760 h/yr = 24,680 MTONne/yr CO₂.

3.6.4.2 Energy Requirement for NaOCl: Since 4.4% of the chlor-alkali reaction is used to produce bleach through the reaction 2NaOH + Cl₂ => NaOCl + NaCl + H₂O; then 4.4% of the power can be removed from the generation of CO₂.; 4.4% * 21.93MW = 0.96MW
And the potential CO\textsubscript{2} not being emitted is: 0.96 MW * 1MTonne CO\textsubscript{2} / 2.3533 MWh * 8760 h/yr = 3592 Mtonne /yr CO\textsubscript{2} reduction

3.6.4.3 Energy Requirements for NaHCO\textsubscript{3} Produced by the competing Solvay Process

During the NETL/DOE examination period for Phase 1, the Life-Cycle Analysis, the carbon-impact calculations, etc. were reviewed by the NETL team with particular respect to the “world-wide” potential impact; multiple query-and-answer points reinforced that the technologies sought are not “US only”. This resulted in Skyonic Corporation estimating the Life Cycle impact of bicarbonate production against the Solvay process, which is the predominant production process worldwide. Skyonic Corporation has conferred with several “trona-miner” companies and our internal rough estimates of their processing are that the mining and refining process is likely more carbon intensive even than the Solvay process, though exact figures for the minority of production by mining trona do not exist.

7.7-10.8 GJ/t Electricity + Fuels & 2.2-2.8 GJ/t Kiln fuel

Since direct mining of trona produces sesquicarbonate, not bicarbonate, the bulk chemical process for the manufacture of NaHCO\textsubscript{3} is the Solvay process.\textsuperscript{13}

\begin{align*}
1) & \quad \text{NaCl} + \text{H}_2\text{O} + \text{NH}_3 = \text{NaCl} + \text{NH}_4\text{OH} \\
2) & \quad 2\text{NH}_4\text{OH} + \text{CO}_2 = (\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O} \\
3) & \quad (\text{NH}_4)_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} = 2\text{NH}_4\text{HCO}_3 \\
4) & \quad 2\text{NH}_4\text{HCO}_3 + 2\text{NaCl} = 2\text{NaHCO}_3↓ + 2\text{NH}_4\text{Cl} \\
5) & \quad \text{Then the precipitating NaHCO}_3\text{is filtered and converted to Na}_2\text{CO}_3 \text{thermally.} \\
6) & \quad 2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{CO}_2↑ + \text{H}_2\text{O} \text{(this recycles the CO}_2) \\

\text{The CO}_2 \text{needed for the reaction is obtained from the decomposition of CaCO}_3 \text{ (CaCO}_3 = \text{CaO} + \text{CO}_2↑) \text{ and the NH}_3 \text{ is recovered by the addition of Ca(OH)}_2 \\
7) & \quad \text{CaO} + \text{H}_2\text{O} = \text{Ca(OH)}_2 \\
8) & \quad \text{Ca(OH)}_2 + 2\text{NH}_4\text{Cl} + \text{CaCl}_2 + 2\text{NH}_3↑ + \text{H}_2\text{O} \text{(this recycles the NH}_3) \\
9) & \quad \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} = 2\text{NaHCO}_3 \\

\text{Using data published by the European Soda Ash Producers Association, the energy requirement for this process is composed of two components:}

\text{Using Average Values}

1) For the kiln 2.5 GJ/tonne \text{Na}_2\text{CO}_3 \\
2) For the remainder of the process 9.25 GJ/tonne of \text{Na}_2\text{CO}_3

\textsuperscript{13} \text{ESAPA – European Soda Ash Producers Association, Issue N°: 3 Date of issue: March 2004 p. 21, p. 48, Obtain from the link http://www.cefic.be/files/Publications/ESAPA_Soda_Ash_Process_BREF3.pdf}
Convert the basis from Na$_2$CO$_3$ to NaHCO$_3$

Given:

1) molecular weight of Na$_2$CO$_3$ = 106,
2) molecular weight of NaHCO$_3$ = 84,
3) two moles of NaHCO$_3$ are created from one mole of Na$_2$CO$_3$ via the reaction
   Na$_2$CO$_3$ + CO$_2$ + H$_2$O = 2NaHCO$_3$
4) The ratio of the basis of NaHCO$_3$ : Na$_2$CO$_3$ = 2(84/106) = 1.585 tonne NaHCO$_3$/tonne Na$_2$CO$_3$

The power and CO$_2$ generated from the kiln is calculated as follows:

Given that a typical kiln is powered by coal
1) From the Kiln Solvay Avg = 2.5 GJ/Tonne Na$_2$CO$_3$
2) 2.5 GJ/Tonne Na$_2$CO$_3$ * (1/1.585) = -1.577 GJ/Tonne NaHCO$_3$
3) lb.CO$_2$ generated per MMBTU energy of coal = 227.4 lbs CO$_2$/MMBTU

-1.577 GJ/tonne NaHCO$_3$ *0.9478 MBTU/GJ *227.4 lbs CO$_2}$/MBTU * (1/80% efficiency)*
(1/2206 tonnes/lb ) *151,740 tonnes/yr. NaHCO$_3$ = -29,230 tonne/yr. CO$_2$

3.6.5 Power for Balance of Plant

For the remainder of the plant, the average power requirement is a mixture of electricity and fossil fuels. The requirements will be calculated both ways and averaged.

First change the basis to NaHCO$_3$ 9.25 GJ/Tonne Na$_2$CO$_3$ * (1/1.585) = -5.835 GJ/Tonne NaHCO$_3$

Assuming the fossil fuel method:

-5.835 GJ/Tonne GJ/tonne NaHCO$_3$ *0.9478 MBTU/GJ *227.4 lbs CO$_2$/MBTU * (1/80% efficiency)*
(1/2206 tonnes/lb ) *151,740 tonnes/yr. NaHCO$_3$ = -108,150 tonne/yr CO$_2$

Assuming the calculation is based on electric power:

5.835 GJ/tonne * 151,740 tonnes NaHCO$_3$ * (1yr/8760 hr)*(1 hr/3600 sec) 1000 MW/GW = 28.08 MW

Converting this to CO$_2$ generated:

28.08 MW x 8760 hr/yr * (1/2353) Tonne/kwh *1000kw/MW= -104,540 tonne CO$_2$/ yr.
Average the two values: -106,350 tonne CO$_2$/yr.

However the manufacture of NaHCO$_3$ requires some additional process steps, namely an additional CO$_2$ absorption followed by a filtration and a drying. Using estimated values, the additional energy for each additional step is: Absorption column 0.60 MW; Centrifuge 0.25 MW; Dryer 0.15 MW; Sum = ~1.00 MW

1 MW x 8760 hr/yr * (1/2353) Tonne/kwh *1000kw/MW= -3723 tonne CO$_2$/yr.

**Total CO$_2$ in std NaHCO$_3$ production** = -(29,230 + 106,350 + 3723) = 139297.8706 ~ = -139,300 tonne CO$_2$/yr.

### 3.6.6 Waste water

These calculations are similar to calculations for CO$_2$ associated with obtaining makeup process water, and are attributable to electricity to pump the water. Based on the plant requirement 67.32 GPM or 4032 Gallons/hour of waste water and 2232 kwh/Million Gallons energy requirement for sewage: \(^{14}\) Energy requirement = 4032 gallons/hr * 2232 kwh/Million Gallons * 10^-6 = 9.00 kw; CO$_2$ emissions (waste water pumping) = (9.0 kw)(1/2004 tonne/kwhr)*8760 hr/yr = 39.3 tonne CO$_2$/yr

Calculation of Energy-Recovery from Hydrogen/Nat-gas Effects: The SkyMine® pilot plant project at SkyMine® does not include a natural-gas turbine; it is beyond the scope of this project to sell hydrogen gas directly to market and buy displaced natural gas and partially self power the unit with electricity so self generated; the facts of natural gas reformation into hydrogen, and the technology of natural-gas turbines generating electricity are well established processes for which the funding of such would be inefficient. (Obtained from Life Cycle Assessement of Hydrogen Production via Natural Gas Steam Reforming, Feb 2001, Spath, Mann From executive summary page 6.)

Under energy balance:

Given 0.66 MJ H$_2$ per 1 MJ Natural Gas and 142 MJ/kg for H$_2$ and 54 MJ/kg for natural gas

For H$_2$ 0.59MJ/(142 MJ/kg) = 0.004155 kg; For Natural Gas 1MJ/54MJ/kg = 0.018519 kg

Natural Gas : H$_2$ = 0.018519/0.004155 = 4.45

[NOTE: many industry references will claim a nat-gas::hydrogen ratio around 3.5::1. These ratios include only the natural gas consumed in the process itself, and do not account for the natural gas combusted to produce steam and degrees of superheat used in the reaction, for the reason that the steam is typically used for other purposes or sourced from existing operations at a refinery. Fully accounting for the total natural gas consumed (as Spath/Mann do in the EIA study) is the proper measure.]

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\(^{14}\) San Antonio Water Supply -- Obtained from the link
3.6.7 Net Electricity/Carbon Emissions

Using the same format as the Phase 1 application to summarize the net electricity and carbon-emission effects of the SkyMine® process itself and its upstream and downstream effects, the following two tables illustrate its carbon capture, using the native CPS San Antonio power system carbon intensity for power input, and varying the assumed recovery efficiency between 45% (US national Nat-gas average) and 60%, a figure chosen to represent attainable best available nat-gas efficiencies.

<table>
<thead>
<tr>
<th>SkyMine® Power and Carbon Summary 45% Nat. Gas Efficiency (US Average)</th>
<th>Power (MW) (-) = reduction</th>
<th>Carbon Dioxide MT/yr (-) = reduction</th>
<th>Carbon Dioxide Cumulative MT/yr (-) = reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Carbon Capture</td>
<td>-76,488</td>
<td>-76,488</td>
<td></td>
</tr>
<tr>
<td>Power Consumed (+)/Recovered (-)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrochemical Plant</td>
<td>14.25</td>
<td>53,046</td>
<td>-23,442</td>
</tr>
<tr>
<td>Transport Inputs &amp; Makeup water</td>
<td></td>
<td>4,300</td>
<td>-19,142</td>
</tr>
<tr>
<td>Hydrogen/Natural Gas</td>
<td>-6.63</td>
<td>-24,680</td>
<td>-43,822</td>
</tr>
<tr>
<td>Power Saved From Chemical Production (-)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl₂</td>
<td>-22.42</td>
<td>-83,459</td>
<td>-127,281</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>-28.57*</td>
<td>-139,300</td>
<td>-266,581</td>
</tr>
<tr>
<td>Transp. of Outputs and wastewater</td>
<td></td>
<td>4500</td>
<td>-262,081</td>
</tr>
</tbody>
</table>

Table 3.21 – Summary Results #1
<table>
<thead>
<tr>
<th>SkyMine® Power and Carbon Summary 60% Nat. Gas Efficiency (BAT)</th>
<th>Power (MW) (-) = reduction</th>
<th>Carbon Dioxide MT/yr (-) = reduction</th>
<th>Carbon Dioxide Cumulative MT/yr (-) = reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Carbon Capture</td>
<td></td>
<td>-76,488</td>
<td>-76,488</td>
</tr>
<tr>
<td>Power Consumed (+)/Recovered (-)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrochemical Plant</td>
<td>14.25</td>
<td>53,046</td>
<td>-23,442</td>
</tr>
<tr>
<td>Transp. of Inputs and Makeup water</td>
<td></td>
<td>4,300</td>
<td>-19,142</td>
</tr>
<tr>
<td>Hydrogen/Natural Gas</td>
<td>-8.82</td>
<td>-32,833</td>
<td>-51,975</td>
</tr>
<tr>
<td>Power Saved From Chemical Production (-)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl₂</td>
<td>-22.42</td>
<td>-83,459</td>
<td>-135,434</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>-28.57*</td>
<td>-139,300</td>
<td>-274,734</td>
</tr>
<tr>
<td>Transp. of Outputs and wastewater</td>
<td>4500</td>
<td></td>
<td>-270,234</td>
</tr>
</tbody>
</table>

*Combination of power and heat. See detailed calculations above.

Table 3.22 – Summary Results #2

3.6.8 Energy Use, Carbon -Intensity, and Use of Renewable Non-Carbon Power for Decarbonation

During our interactions with DOE/NETL examiners, it was stated that “the reduction could be further increased by the use of renewable energy which the applicant states is a nearby resource.” The effect of this energy usage on carbon penalty is explored.

Note: On Table 3.8 above, the “SkyMine Power and Carbon Summary: 60% Nat. Gas Efficiency (BAT)” does not take into account any of the carbon reduction in chemical markets, e.g. NaHCO₃ or Cl₂. The basic carbon capture process can be simply expressed in these steps:

(A) 76,448 tonnes of CO₂ are captured and mineralized.

(B) 53,046 tonnes of CO₂ are produced in generating the power to do so at the CPS average carbon-intensity of 2050 kWh/tonne-CO₂ (937.8 lb CO₂/MWh).

(C) Accounting for transportation and production of Raw materials and water usage, further lowers the apparent carbon reduction to 19,143 tonnes of CO₂.
Accounting for power generated by natural-gas displaced as a feedstock by shipping hydrogen to market adds back 8.82MW of net US power at no additional CO₂ increase, resulting in a net reduction of 51,975 tonnes CO₂.

NOTE: If the power-mix used to power the SkyMine® has a carbon-intensity identical to natural gas, then the carbon-penalty for this single case is the simple ratio of the net-carbon reduction (51,975) divided by the carbon-mineralized; i.e. penalty = 1 – (51,975/75,000) = 30.7%.

This single example will vary, depending upon the carbon intensity of the input power and the chosen value for natural-gas turbine efficiency: i.e. this generalized example allows a point-of-reference for discussing these factors:

(i) The SkyMine® process is indifferent to the source of the carbon dioxide or its carbon/power intensity; indeed, at the SkyMine® plant, the source CO₂ generates no power at all, as the host-site is a cement plant.

(ii) Item (B) varies depending upon the carbon-intensity of the grid powering the SkyMine® plant: If the 14.25 MW were produced entirely by non-carbon power sources, this term would drop to zero, and the net carbon reduction would go to 105,000 tonnes per year.

(iii) Another factor in determining the carbon-penalty of a SkyMine® is the efficiency with which conserved natural gas is used for power production instead of for industrial hydrogen production. In the example in the table below, the efficiency (using HHV) is 45%. In the United States, a range of natural-gas efficiencies exist, from low grade single effect units, to the higher national average, to the highest turbine one can normally purchase with high efficiency, to the limits of best available technology (BAT), which are approximately 60% of HHV. Clearly, the higher the efficiency of natural gas power production is, the higher will be term (C) and the lower the penalty.

### 3.6.9 Effects of Partial Renewable Energy Feed and Basis Natural Gas Turbine Efficiency on SkyMine® Carbon Penalty

The following chart illustrates the effects mentioned above; increasing the input power to the SkyMine® that derives from renewable sources lowers carbon penalty; increasing the efficiency of natural gas turbine efficiency that operates to convert displaced natural gas into electricity lowers carbon penalty.
This graph depicts several important relationships useful in understanding the impact of SkyMine\textsuperscript{®} technology and its path of future development without internal improvements in the SkyMine\textsuperscript{®} technology itself. The light green area represents a region of operation that is of interest in describing SkyMine\textsuperscript{®} energy penalty.

\textbf{3.6.10 CONCLUSIONS FROM LIFECYCLE ANALYSIS}

First, it is important to note that the expected operating range of the proposed pilot plant is competitive to other methods of carbon capture and sequestration and that the proposed plant can achieve such with off-the-shelf equipment, run in a particular process sequence, in a patent protected process.

Second, as increased renewable power and higher gas power efficiencies are implemented nationally, the energy penalty of the technology will decrease, without further “internal” improvements in SkyMine\textsuperscript{®} efficiencies beyond the proposed pilot.

Third, while the above points out how the SkyMine\textsuperscript{®} technology is to benefit from the national objectives of higher grid efficiency and lower grid carbon intensity, it is also clear that the first pilot plant proposed in this application will improve in future implementations along these lines:

\begin{itemize}
  \item[(A)] Improvement in SkyMine\textsuperscript{®} input power efficiencies beyond plan for pilot-plant:
    \begin{itemize}
      \item Reducing AC/DC losses (estimated in plan at 0.5%)
      \item Increasing current-efficiencies (estimate in plan at 2%)
    \end{itemize}
\end{itemize}
c. Reduction of brining/acidification parasitic loads

(B) Reduction in SkyMine® power consumption in electrolytic base generation
   a. Secular improvement in electrolyzer electrodes and membranes
   b. As practiced optimization of matching new revision electrodes and membranes for best performance in SkyMine® operation regime/corner.
   c. Multi-variant optimization of plant inputs (state variables, concentrations, flow rates, control schemes) to enhance performance.

(C) Efficient use of bases so-generated for carbon capture
   a. Driving gas-liquid contact machines to achieve near-one-point-oh Na:C ratios, i.e. mostly NaHCO₃ formation, whereas Na₂CO₃ has a Na to C of 2:1.

(D) Efficient means of separating water from crystalline bicarbonate
   a. More efficient water removal techniques at higher flux/greater rejection rates
   b. Reduction in final dry-drive reactions to achieve low Na:C ratios

(E) Maximizing interaction with host-plant
   a. Heat transfer to best use
   b. Generation of low grade steams to replace mechanical energies further

These are some of the first-categories for further research and development of the SkyMine® process fundamentals. Skyonic Corporation looks to measure the losses and inefficiencies in these categories at scale in the pilot plant, and to project for further R&D the best leverage items that will direct the development path for this promising means of carbon capture and permanent mineral sequestration.

3.7 SAFETY

A high-level safety analysis, using OSHA Regulation 29 CFR 1910.119 as a guideline, was performed in Phase 1. Although this facility is not subject to OSHA PSM guidelines, a Comprehensive Process Safety Management procedures (HAZOP) review started in Phase 1 (32 of 45 non-chlor-alkali P&IDs reviewed) will be completed in Phase 2. The plant is being designed with redundant control and monitoring systems, alarms, and communications capability throughout the site. Lines containing chlorine are designed to minimize the volume of chlorine on-site under normal operating conditions. Chlorine produced in the process is combined with hydrogen to produce hydrochloric acid (HCl), and mixed with water during this combination to eliminate safety concerns. Excess chlorine is immediately combined with a side stream of caustic to form bleach, another beneficial product produced in the SkyMine® process. A secondary bleach system provides for controlled shut down of the electrolysis system.

3.8 SUPPLY CHAIN

During this phase of the project, feed stock products were sampled, and approved for the process by means of compositional chemical analysis. Prior to the start of construction, Skyonic has identified two independent salt suppliers with similar, if not identical, purity levels. The Project Team, assisted by a supply-chain consulting firm, completed an extensive supply chain study for the feedstock salt. Follow-up meetings and visits in Phase 1 took place at supplier facilities and with third-party logistics (3PL) providers, and dialogue is ongoing. This activity will
ensure a reliable and timely flow of raw materials to the pilot plant as well as assist in planning the outflow of output products from the plant to purchasers.

3.9 PROJECT MANAGEMENT

Throughout Phase 1, the Project Team managed the work breakdown structure (WBS) to two levels beyond reporting requirements to most effectively monitor and control the schedule and costs of activities and to develop the tools that will well-position the team for the construction phase of the project. All project costs, including labor, have been documented on a weekly basis. Engineering hours for these stages of design were measured against standard industry benchmarks. Effective paths of communication have been established with all project stakeholders, and reporting has been comprehensive and timely. The project has consistently met NETL/DOE requirements and requests and all required reports have been submitted to NETL/DOE on schedule.

4.0 RESULTS & DISCUSSION

The collaborative efforts of the Project Team and support entities have resulted in the design for a pilot SkyMine® plant that meets the project’s stated objectives, and a detailed plan for building and operating the plant at the Capitol Aggregates’ Cement Plant in San Antonio, Texas in Phase 2 of the project. Design products include preliminary design of processes, civil engineering, buildings, mechanical systems, electrical systems, and overall project management. Preliminary detailed design products cover the above systems, as well as contractor selection for building and construction, review of constructability, and development of a sourcing plan for process equipment.

4.1 Process Analysis & Characterization

Flue Gas Conditioning – Empirical Results

Flue gas samples were collected at the host site from June to October 2010. These samples allowed the engineers to develop a design profile of the gas content and temperature fluctuations over an extended period. As the ambient temperature increases in the summer months, the coal composition changes which can be seen as trending components in flue gas. Table 4.1 shows the summary of the collected composition data.
**Capitol Cement Flue Gas Composition Analysis**

<table>
<thead>
<tr>
<th></th>
<th>% O2</th>
<th>% CO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>10.22</td>
<td>19.34</td>
</tr>
<tr>
<td>Standard Error</td>
<td>0.07</td>
<td>0.13</td>
</tr>
<tr>
<td>Median</td>
<td>10.13</td>
<td>19.42</td>
</tr>
<tr>
<td>Mode</td>
<td>10.24</td>
<td>18.83</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.73</td>
<td>1.42</td>
</tr>
<tr>
<td>Sample Variance</td>
<td>0.53</td>
<td>2.02</td>
</tr>
<tr>
<td>Kurtosis</td>
<td>-0.20</td>
<td>-0.37</td>
</tr>
<tr>
<td>Skewness</td>
<td>0.42</td>
<td>-0.26</td>
</tr>
<tr>
<td>Range</td>
<td>3.70</td>
<td>7.03</td>
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<tr>
<td>Minimum</td>
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<td>15.74</td>
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<tr>
<td>Maximum</td>
<td>12.06</td>
<td>22.77</td>
</tr>
<tr>
<td>Count</td>
<td>111.00</td>
<td>111.00</td>
</tr>
</tbody>
</table>

**Table 4.1 Summary of Flue Gas Data**

This data was used to create maximum and minimum cases to ensure the equipment and line sizing was suitable for all cases. Also testing was performed in the absorption columns with flue gases containing both higher and lower CO₂ fractions to predict any instability in the system equilibrium. As discussed above, trending in the flue gas compositions is an indication of the variance. Figures 4.1 and 4.2 show the composition of CO₂ and O₂ over the testing period.
Figure 4.1 %CO₂ in Flue Gas vs Time
The general data trending is the direct result of the mixture of high and low grade coal for combustion. The high variance in %CO₂ and %O₂ in a short time span is attributed to the source of the flue gas at the host site. Oxygen is a non-reacting component of the flue gas in this system. During normal operation, the flue gas is a mixture of exhaust from the kiln and exhaust from the mill. On average, the CO₂ fraction of the flue gas is 18-19%. The mill actually dilutes the CO₂ concentration by a few percent when it is running. The mill sporadically comes on and off line which gives a variation of %CO₂ that can be seen even in data taken as often as hourly. The absorption columns show a very high ability to adapt to the fluctuations in %CO₂. The first generation columns at the field test unit had a 14-minute retention time and proved the CO₂ capture efficiency was unaffected by the small variances as long as the average CO₂ to carbonate molar ratio was greater than 1. During the pilot operation, flue gas will be constantly measured to maintain system stability. Communication between the host site and Skyonic will enable smoother transitions and adjustments on the larger scale.

**Flue Gas Conditioning – Simulation Results**

One very useful function of Aspen Plus is the sensitivity analysis. This allows multiple set points to be tested on a model to graphically analyze that variable’s effect on the areas in the system specified by the user. In the flue gas conditioning step, the goal was to maximize removal of...
heavy metals, and SOx and NOx with the least amount of energy consumption. Using the sensitivity analysis, a condensation curve was generated as seen in Figure 4.3.

![Condensation Curve](image)

**Figure 4.3 Condensation Curve**

The sensitivity analysis varied temperature from 255°F down to 90°F. Condensate begins to form at approximately 140°F and condensation continues as the temperature decreases. Mercury is removed from the flue gas stream with the condensed vapor. Aspen does not give much assistance on mercury because of the many compounds formed when mercury is in the liquid phase with sulfates and nitrates. This is why the mercury in the graph does not have a smooth curve. 104°F was chosen as the optimum temperature for absorption purposes and at this temperature 70% of the water vapor in the flue gas is condensed.

A higher flue gas temperature fed to the carbonate column raises the column temperature and therefore the scrubbed exhaust stream contains more water vapor. This water loss must be balanced up by adding water to the caustic, and reducing the NaOH concentration fed to the column. In the case of low water, carbonate precipitates can form in the packed carbonate column and cause fouling of the packing and downstream equipment; this must be avoided. The water balance of the plant is critical for maintaining concentrations of carbonate and bicarbonate, preventing decahydrate formation, preventing plugged packing, and for accurately sizing equipment.
**CO2 Absorption—Empirical Results**

To characterize and improve the SkyMine® process, the three main process variables, i.e. Gas Flow Rate; Recirculation Rate; and NaOH Concentration, were tested in the set up configuration shown in Figure 3.6. The dependent variables are CO₂ absorption, pH of the liquor, and bicarbonate and carbonate concentration. The CO₂ absorption efficiency is calculated by sampling the inlet and outlet percentage of CO₂ in the gas stream. This is calculated for each individual column as well as for the total system. The biggest contributor to CO₂ absorption is pH, specifically the amount of free OH⁻. The free NaOH reacts with the CO₂, removing it from the gas stream. The more CO₂ that is reacted, the less NaOH in the fluid, and thus a lower pH.

The first set of experiments focused on gas flow rate. Three settings (8, 10, and 12 scfm) were investigated. Mid was set at 10 scfm. The recirculation rate on each of the pumps was set to 4 gpm and the NaOH feed concentration was set at 10%.

The second experiment examined the recirculation rate of the fluid. The recirculation rate was increased to 5 gpm on all the columns and the gas flow rate was varied from 8 to 10 to 12 scfm. Because of the two different diameters of the two types of columns, increasing the recirculation from 4 to 5 gpm did not have the same affect. To better equate the two recirculation rates between the columns, the recirculation rate of the two larger diameter columns (Columns 1 & 2) was increased from 4 to 10 gpm. At this setting the superficial liquid velocity is similar in both columns.

Finally, the tests were repeated with a 20% sodium hydroxide concentration.

*Gas Flow (8, 10, 12 SCFM), Low Recirculation Rate (4 GPM), 10% NaOH*

<table>
<thead>
<tr>
<th>Gas Flow SCFM</th>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
<th>Column 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>Absorption</td>
<td>pH</td>
<td>Absorption</td>
</tr>
<tr>
<td>8</td>
<td>8.46</td>
<td>8%</td>
<td>9.94</td>
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<td>8</td>
<td>8.42</td>
<td>2%</td>
<td>9.45</td>
<td>12%</td>
</tr>
<tr>
<td>Average</td>
<td>8.44</td>
<td>5%</td>
<td>9.45</td>
<td>12%</td>
</tr>
<tr>
<td>10</td>
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<td>9.58</td>
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<td>10</td>
<td>8.46</td>
<td>4%</td>
<td>9.44</td>
<td>15%</td>
</tr>
<tr>
<td>Average</td>
<td>8.46</td>
<td>11%</td>
<td>9.45</td>
<td>12%</td>
</tr>
<tr>
<td>12</td>
<td>8.64</td>
<td>21%</td>
<td>9.40</td>
<td>30%</td>
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<tr>
<td>12</td>
<td>8.66</td>
<td>13%</td>
<td>9.44</td>
<td>9%</td>
</tr>
<tr>
<td>12</td>
<td>8.77</td>
<td>10%</td>
<td>9.46</td>
<td>8%</td>
</tr>
<tr>
<td>Average</td>
<td>8.72</td>
<td>16%</td>
<td>9.45</td>
<td>10%</td>
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</table>

Table 4.2 CO₂ Process Variables
Low, Mid, High Gas Flow, High Recirculation Rate (5 GPM), 10% NaOH

<table>
<thead>
<tr>
<th>Gas Flow</th>
<th>Column 1</th>
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<th>Column 4</th>
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<tbody>
<tr>
<td></td>
<td>pH</td>
<td>Absorption</td>
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<td>Absorption</td>
</tr>
<tr>
<td>7.5 scfm</td>
<td>8.35</td>
<td>-1%</td>
<td>9.39</td>
<td>16%</td>
</tr>
<tr>
<td>10 scfm</td>
<td>8.47</td>
<td>14%</td>
<td>9.48</td>
<td>11%</td>
</tr>
<tr>
<td>12 scfm</td>
<td>8.56</td>
<td>15%</td>
<td>9.40</td>
<td>8%</td>
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</table>

Table 4.3 CO₂ Process Variables, 5GPM/10% NaOH
Low Gas Flow (8 SCFM), High Recirculation Rate (5 GPM), 20% NaOH

<table>
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<tr>
<th></th>
<th>Column 1</th>
<th>Column 2</th>
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<th>Column 4</th>
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</thead>
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<tr>
<td>Sample 1</td>
<td>pH</td>
<td>Absorption</td>
<td>pH</td>
<td>Absorption</td>
</tr>
<tr>
<td></td>
<td>8.46</td>
<td>33%</td>
<td>9.60</td>
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<tr>
<td>Sample 2</td>
<td>8.46</td>
<td>11%</td>
<td>9.56</td>
<td>10%</td>
</tr>
<tr>
<td>Sample 3</td>
<td>8.45</td>
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<td>12%</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>18%</td>
<td></td>
<td>11%</td>
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Table 4.3 CO₂ Process Variables, 5GPM/20% NaOH
High Gas Flow (12 SCFM), High Recirculation Rate (5 & 10 GPM), 20% NaOH

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td></td>
<td>pH</td>
<td>Absorption</td>
<td>pH</td>
<td>Absorption</td>
<td>pH</td>
<td>Absorption</td>
<td>pH</td>
<td>Absorption</td>
</tr>
<tr>
<td>Sample 1</td>
<td>8.35</td>
<td>18%</td>
<td>9.64</td>
<td>6%</td>
<td>12.08</td>
<td>30%</td>
<td>11.39</td>
<td>29%</td>
</tr>
<tr>
<td>Sample 2</td>
<td>8.26</td>
<td>8%</td>
<td>9.61</td>
<td>9%</td>
<td>11.96</td>
<td>36%</td>
<td>11.22</td>
<td>31%</td>
</tr>
<tr>
<td>Sample 3</td>
<td>8.32</td>
<td>12%</td>
<td>9.78</td>
<td>10%</td>
<td>13.60</td>
<td>37%</td>
<td>13.79</td>
<td>30%</td>
</tr>
<tr>
<td>Sample 4</td>
<td>8.29</td>
<td>7%</td>
<td>9.69</td>
<td>12%</td>
<td>13.41</td>
<td>32%</td>
<td>13.66</td>
<td>35%</td>
</tr>
<tr>
<td>Average</td>
<td>8.29</td>
<td>11%</td>
<td>9.69</td>
<td>9%</td>
<td>13.41</td>
<td>34%</td>
<td>13.66</td>
<td>31%</td>
</tr>
</tbody>
</table>

Table 4.4 CO₂ Process Variables, 5 & 10GPM/20% NaOH
The biggest influence on absorption was pH, which was known prior to testing. As pH increased, CO₂ absorption increased. Increased recirculation rate absorption did not impact CO₂ absorption. The liquid distributors proved capable of handling larger recirculation rates without compromising column performance. Similar distribution will be employed in the larger pilot scale carbonate columns as opposed to spray nozzles. This should improve plant uptime. In two different instances, Columns 1 and 3 had bicarbonate and carbonate precipitation. Bicarbonate precipitation will be investigated further in a larger bubble column that is being constructed as part of the project.
**CO₂ Absorption— Simulation Results**

In running Aspen simulations, in parallel with the field test unit, empirical data allowed adjustments to be made to produce more accurate models. In the packed columns, empirical data for efficiency, concentrations, and pH were the critical parameters in generating the model. Figure 4.13 shows the comparison of the Aspen generated data to the empirical results before adjustments were made.

![Mass Concentration vs pH](image-url)

**Figure 4.13 pH Comparison of Aspen vs Empirical Data**

The figure above shows the carbonate to bicarbonate concentration as the pH changes. In the absorption process, a carbonate solution (pH of 11) is converted to a mostly bicarbonate solution (pH of 9). Figure 4.13 shows the transition from carbonate ions (CO₃--) to bicarbonate ions (HCO₃-) as the pH decreases. When initially comparing the empirical data to the Aspen data, the curves favored one another, but the Aspen data was shifted by -1.1 on the pH scale. This was found to be a result of Aspens default reaction efficiency, which assumes ideal conditions. When the empirical data from Figure 4.14 is compared to the data from literature in Figure 3.2, one can clearly see that the empirical data is not flawed. The pH calculated in Aspen was corrected with the help of the Aspen technical support and now represents the empirical data and literature. This was adjusted in the Radfrac block efficiency which led to a more accurate model shown in Figure 4.14. The pH indicated in the process flow diagrams were
produced with the corrected Aspen simulation. pH measurements were checked with redundant pH probes which were calibrated weekly.

![Mass Concentration vs pH](image)

**Figure 4.14 Corrected pH Comparison of Aspen vs. Empirical Data**

Using the method above to accurately model the field test unit in Aspen, scale up to the pilot plant column was a matter of capacity since the reaction chemistry and efficiencies were characterized. The capacities on the pilot plant scale were introduced to the model and the generated output allowed the engineers to confirm equipment sizes with the equipment vendors.

On the pilot plant scale simulation, other major pieces of equipment were added to the column models so a global perspective of the process could be developed. Hundreds of sensitivity analyses were performed to tweak and trim the model to run as lean and efficient as possible. When all performance criterion were met, the Aspen model was ported into excel where the material balance was created. Figure 4.15 shows a sensitivity analysis performed in Aspen, which shows the effect of varying the flue gas flow rate for a specified carbonate flow rate and the resulting CO₂ capture efficiency and liquor concentration.
As seen in the graph, the bicarbonate to carbonate ratio of the liquor increases with the addition of flue gas. This correlates with a downward trending pH and capture efficiency. This test parallels the empirical data collected at the field test unit, on a smaller scale. This example is just one of hundreds of combinations of column conditions that will be further studied in Phase 2 to optimize the operation of the bubble column.

**4.2 Facility/Site Plan**

Engineering documentation completed during Phase 1 includes a myriad of process flow diagrams (PFDs), piping and instrumentation diagrams (P&IDs), material and energy balances, major equipment listings, specifications, and data sheets.

Significant process work helped to advance/optimize SkyMine® processes as elaborated for commercial demonstration scale.

Laboratory work and process simulation in the areas of chemical precipitation and dewatering, have allowed for the simplification of processes, and the reduction of capital equipment requirements and operating costs. Specific advances made in this area during Phase 1 are as follows:
• Improved recycle loops, which minimize water consumption and will reduce final product waste;
• Modeled various configurations of dissimilar equipment to reduce capital costs;
• Optimized available heat to accelerate final product purification; and
  Provided recirculation of discharge liquid to reduce water consumption and maximize CO₂ use.

4.3 Project Management

Plant visits and discussions with equipment users provided the Project Team with valuable lessons learned, which will be leveraged to control costs and mitigate potential risk issues. Multiple quotes and responses to bid requests allow the team to evaluate costs and performance, and help guide prudent equipment/vendor selection. To the greatest extent practicable, equipment and products purchased with funds made available under this award will be American-made.

Supply chain development from Phase 1 shows that the detailed material handling and logistics plans for both feedstock, and the beneficial use products produced at the San Antonio SkyMine® plant are feasible by leveraging support services currently in place.

Working closely with FB&D, the Project Team developed a detailed Phase 2 Project Management Plan, and identified and customized tools (e.g. EVMS, WBS) to monitor and control the project. The financial team implemented robust accounting systems, which the Defense Contract Audit Agency (DCAA) audited and approved during Phase 1.
5.0 CONCLUSIONS

In Phase 1 of the project, the Project Team and support entities completed a design and plan for building a SkyMine® plant capable of annual capture of 75,000 tonnes (82,687 tons) of emitted CO₂ at a suitable host site in San Antonio, Texas, thereby meeting the primary Phase 1 objectives. All of the necessary components, i.e. process flow diagrams, process verification, site and facility drawings, vendor and host site agreements, environmental permitting plans, and commercial off-take agreements were addressed in Phase 1 to prepare for successful plant construction and process technology testing and demonstration in Phase 2.

All Phase 1 objectives were completed within budget and to schedule with very limited variance. The Project Team identified potential issues of risk, and crafted appropriate mitigation plans. The Project Team has also identified and customized additional tools that will be used to manage the various aspects of Phase 2, and has prepared a detailed Phase 2 Project Management Plan with essential elements, including but not limited to a resource-loaded schedule, project budget, Risk Management Plan, Change Management Plan, and a detailed task listing.

Secondary Phase 1 objectives, like process optimization, construction planning, and supply chain development, were also met. Advanced process modeling and simulation combined with laboratory experiments, proven principles of basic chemistry and well-known electro-chemical processes, and field validations show that the innovative SkyMine® pilot project will achieve its objectives by capturing and mineralizing CO₂. Significant additional benefit is derived from SkyMine®’s capability for removing SOₓ and NOₓ and heavy metals such as Hg from the emitted flue gas.

Analytical results of testing process variables have provided clear optimum values for such items as membrane selection, and pressure and temperature conditions relative to desired flow rates and recovery amounts.

Further, the Life Cycle Analysis that was informed by the logistics of transport of inputs and outputs, concludes that the SkyMine® process is viable over large geographical bounds without disabling transport impediments, and is not limited (as geo-injection processes are) by geologic storage issues. The proposed SkyMine® Pilot Project will capture more than 75,000 tpy of CO₂ from the exhaust gases of a cement kiln. The carbon penalties of the first-plant SkyMine® mineralization process are competitive when compared to other carbon capture technologies. Further improvements in energy penalty range of operation can be achieved by improving SkyMine® internal efficiencies and lowering parasitic loads, which will come about as the project efforts further define the operation of a commercial scale pilot, allowing prioritization of future development efforts.

In matters relevant to the power industry, specifically, the SkyMine® system, in addition to containing its own SOₓ/NOₓ/Metals scrubbing system, has impressive abilities to interact with its input power provider to draw primarily off-peak energy, improve system carbon intensity, and absorb bursts of renewable power.
The SkyMine® technology, built primarily from proven commercial systems, is robust, can be retrofitted to existing plants, and is ready to be tested at pilot scale in preparation for deployment at full commercial scale. Because a SkyMine® plant can be constructed from commercially available sub-components, the design is valuable in establishing a reference plant design that is easily replicable, and can be rapidly down-costed by utilizing the marginal cost of each additional unit. With the achievement of all Phase 1 goals and objectives, the Project is now fully ready to proceed to Phase 2 for final detailed design, construction, and testing and operation of a pilot scale SkyMine® facility that will demonstrate the feasibility of the SkyMine® carbon capture technology at commercial scale.