CAPTURE AND CAPTURE/SEQUESTRATION OF CARBON DIOXIDE

The CEC/MTU Clearite Carbon Dioxide Capture/CO_2 Production Process

Capture of CO_2 Using Commercially Available Chemicals
Sequestration of CO_2 with North Dakota Lignite Fly-Ash
Production of CO_2 for Oil Field Enhancement

Submitted to: **North Dakota Lignite Research Council**

Submitted by: **Carbontec Energy Corporation (CEC)**
Michigan Technological University (MTU)

Date: **April 1, 2016**

BACKGROUND

Carbontec Energy is a developer of technology for the energy, oil, iron, steel and diesel engine industries. Carbontec's business plan is to develop and commercialize the technologies by itself or through establishing joint ventures that own and operate the production facilities, or in some cases, license the technologies. Carbontec Energy has developed technologies in the energy field that have been commercialized in plant facilities that have produced more than $1,300,000,000 in bottom line earnings for investors including a major Wall Street firm and a large utility.

Carbontec Energy Corporation, in cooperation with Michigan Technological University has developed the Patented (Pat. No.US7,919,064B2) CEC/MTU Clearite Carbon Dioxide Capture/Sequestration Process. Carbontec Energy Corporation holds the exclusive world-wide license to utilize and market this patented CO_2 technology.

ABSTRACT

The investigators are developing a new, patented technology for capturing CO_2 from power plant exhaust gases, and reacting it with heat and a catalyst to regenerate the original capture solutions while producing a high quality Carbon dioxide (CO_2) as a product suitable for enhancing oil and gas production. Unlike other methods for capturing CO_2, our Process proceeds at ambient temperature and pressure, and does not therefore need the high pressures that make other methods of CO_2 capture and sequestration so energy-intensive. The regeneration of the original CO_2 capture solutions proceeds at modestly elevated temperatures that simultaneously releases the captured CO_2 for compression and pipeline delivery to the oil fields.

The Carbon Dioxide would have a commercial value estimated at \$20 - \$30+/tonne, that would be used for the enhancement of oil production, providing a profit center for the power generation company.

This proposal describes a test program that would be conducted in the laboratory and pilot facilities of the Chemical Engineering Department of Michigan Technological University, Houghton, Michigan (MTU). This project, described as Phase I, would continue and expand on the earlier laboratory and pilot plant work conducted at MTU and would provide information that would warrant a second and larger project (Phase II) that would demonstrate the use of the technology at a North Dakota Power Generation Plant on a real time pilot plant basis. Phase I would include the fabrication and testing of an additional scrubber, similar to the current MTU/CEC scrubber originally tested. This would allow for the operation of two CO_2 scrubbers in series. This part of the project would be to demonstrate if the addition of a second scrubber could increase the CO_2 capture from a current level of 55% to 70±%.

The CEC/MTU Clearite CO_2 Process uses an alkaline carbonate solution, trade named Clearite VI™ to capture CO_2 from a simulated power plant exhaust gas emission stream. The CO_2 enriched solution is then transferred to a heated CO_2 separation tank. The elevated temperature, and the use of a catalyst, will release the CO_2, for compression and delivery to the CO_2 storage tank. The regenerated Clearite VI™ capture solution is regenerated during the CO_2 production stage and recycled to the Stage I CO_2 capture scrubber unit. It is anticipated that 55% of the CO_2 will be captured in the Stage I CO_2 unit. The emissions from the Stage I unit are transferred to a similar Stage II unit, which is expected to increase the CO_2 capture to 70±%.

The expected result of this work is to determine the reaction kinetics of the CO_2 capture and CO_2 bi-product properties obtained when alkaline carbonate solutions are reacted with CO_2 laden simulated power plant emissions.

During the study of the effect of the concentration levels of carbonate solutions on the removal of CO_2 from the emission stream, on site analyzers will be used to measure and record the CO_2 levels of the CO_2 emission fed into and leaving the CO_2 capture scrubber units.

This and other information generated during this study will be needed to design and operate a Phase II, larger future pilot/demonstration unit that will be placed on-site at an operating North Dakota lignite coal-fired power plant. The work carried out in this project will address two problems in the combustion of North Dakota lignite: (1) It will provide information for a larger, on site pilot/demonstration plant at a North Dakota Lignite fired power generation plant. The overall goal is to provide a means for energy-efficient capture of carbon dioxide, allowing users of North Dakota lignite to meet any future regulations on CO_2 emissions; and (2) It will determine if the process represents a low cost method of extract CO_2 for future compression and pipeline delivery, for the enhancement of oil and gas production, which would help the lignite fired power plants meet their current and future emission regulation requirements at a reasonable cost.

PROJECT SUMMARY

Carbontec Energy Corporation (CEC) in cooperation with Michigan Technological University (MTU) and with the financial support of Great River Energy and other companies is proposing to evaluate the feasibility of carbon dioxide (CO_2) capture and the production of Carbon Dioxide for oil well enhancement with the CEC/MTU Clearite CO_2 Capture/Sequestration Process. The method proposed for evaluation is CO_2 absorption into an alkaline solution to capture the CO_2 followed by the production of pipeline quality CO_2 during the process that would regenerate the original CO_2 alkaline capture solution. This approach when applied in the future on a commercial basis will remove CO_2 from flue gases created during the combustion process at coal fired power plants, while using significantly less energy than other CO_2 capture/sequestration methods. The reduced energy requirement compared to other technologies is due to the elimination of any need for very high heating temperatures or pressurizing solutions or gases. In addition to capturing the CO_2, the sequestration step creates valuable CO_2 bi-product.

This new technology for the Capture and Sequestration of CO_2 uses readily available Carbonate chemicals (trade named Clearite VI™) that are used to react with a 16% CO_2/air mixture in a scrubber. Fifty five percent (55%) of the CO_2 is captured within minutes to produce a new bicarbonate chemical that contains the recovered CO_2. This new chemical is then reacted with a catalyst and heat, which separates the CO_2 as a commercial product. The proposed study will examine the chemistry and reactions in the CO_2 scrubber with a 16% CO_2, 84% air mixture. Separate tests will also be conducted to study the effects that measured additions of SO_2 and other contaminants will have on the Process. The mechanisms involved during the regeneration of the original capture chemical will be studied to determine if the catalyst and heat can not only produce a high quality CO_2 product, but at the same time regenerate a substantial portion of the original Carbonate Capture chemical.

Previous tests conducted in the research laboratories of Michigan Tech used a specially designed single stage scrubber. A second similar scrubber will be fabricated under this program to provide a two stage scrubber unit that will be tested to determine if the CO_2 capture can be increased from the current level of 55% to a higher level.

The work conducted under this program is expected to provide information for a second, future Phase II, during which a larger two stage pilot scrubber, along with the required pumps, sumps, controls and recording equipment will be fabricated and installed to intercept and process a slip stream from the stack of the No.2 unit at Great River Energy's Coal Creek, North Dakota Station. This future pilot scrubber will confirm the tests results obtained during Phase I in the laboratory and pilot scrubber at Michigan Tech and provide information for a commercial installation. **This CO_2 Capture/ CO_2 Production process is further described as follows:**

The first step in the CEC/MTU's Clearite CO_2 Capture/Production process is the absorption of the CO_2. Absorption of the CO_2 takes place in the MTU scrubber in an alkaline aqueous carbonate (CO_3^{-2}) solution which converts it to a bicarbonate (HCO_3^-) solution as it absorbs CO_2. The second step in the process involves the reaction of the bicarbonate solution, created from the absorption step, with a catalyst. The bicarbonate ions reacted with a catalyst when heated, release the CO_2 as a gas, while being converted to the original carbonate solution, which will then be recycled to capture additional CO_2.

One of the potential challenges of this CO_2 Process, a reaction that is carried out at ambient conditions, is to determine if other elements in the emission stream will interfere with or foul the capture of CO_2. This will be studied in the laboratory by the addition of SO_2 and other components into the feed gas stream.

PROJECT DESCRIPTION

Goals and Objectives

On a laboratory and small pilot unit scale, one goal of the project is to capture at least 55% of the CO_2 emitted from a gas stream containing 16% CO_2 at ambient temperature and normal pressure using readily available chemicals. A second goal is to determine if a commercial grade CO_2 product can be produced when the capture chemical is reacted with a catalyst during the regeneration of the original CO_2 capture chemical.

In order to meet the goals of this project the following initial objectives have been identified:

- Conduct CO_2 absorption experiments in different alkaline solutions and compare the cost versus CO_2 absorption rate to determine the best alkaline solution for CO_2 absorption. As mentioned above, small amounts of other contaminants will be added to the CO_2 gas stream to study their effects on CO_2 capture.
- Determine if other products are produced during CO_2 absorption in the chosen alkaline solution.
    - This will involve precipitating solids out of the reacted alkaline solution and then conducting analysis on the solid using TGA, AA, XRD, and SEM
- Conduct CO_2 production experiments reacting the solution created during CO_2 absorption with a varying degree of heat and catalyst.
- A further goal and objective
    - Reaction times will be varied
    - Experiments will be conducted at ambient and elevated temperature conditions

- A further goal and objective is to determine the percentage of the bicarbonate CO_2 solution that can be regenerated by the use of a catalyst that will also release the captured CO_2 as a valuable commercial product.
- Determine the quality of the CO_2 bi-product produced, and if it will require an after treatment to provide the quality needed for oil field enhancement.

CO_2 Process Development – Background

Reagent grade sodium carbonate (Na_2CO_3) was purchased from Sigma-Aldrich and used to create the alkaline solution. Saturation of a Na_2CO_3 solution with CO_2 creates a $NaHCO_3$ solution [1]. The reaction can be seen below in equation (4).

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3 \qquad (4)$$

Experiments were first conducted to determine the amount of Na_2CO_3 in solution that absorbs the highest percentage of CO_2. Results from those experiments showed that a 2% Na_2CO_3 solution, by weight, absorbs the highest percentage of the total CO_2 fed to the solution over time. The composition of the solution was:

- 16.33 grams Na_2CO_3
- 800 grams distilled H_2O

The CO_2 absorption experiments were carried out using the single flask scrubber system described under the work plan section of the proposal. Operating conditions for the absorption experiments are as follows:

- Room temperature
- Atmospheric Pressure
- 16% CO_2 in the gas feed stream
    - 2.57 ml/sec CO_2
    - 14.57 ml/sec Air
- 2% Na_2CO_3 solution by weight in a 1000 ml Erlenmeyer flask
    - 16.33 g Na_2CO_3
    - 800 g distilled H_2O

Results from a CO_2 absorption experiment can be seen below in figure 5.

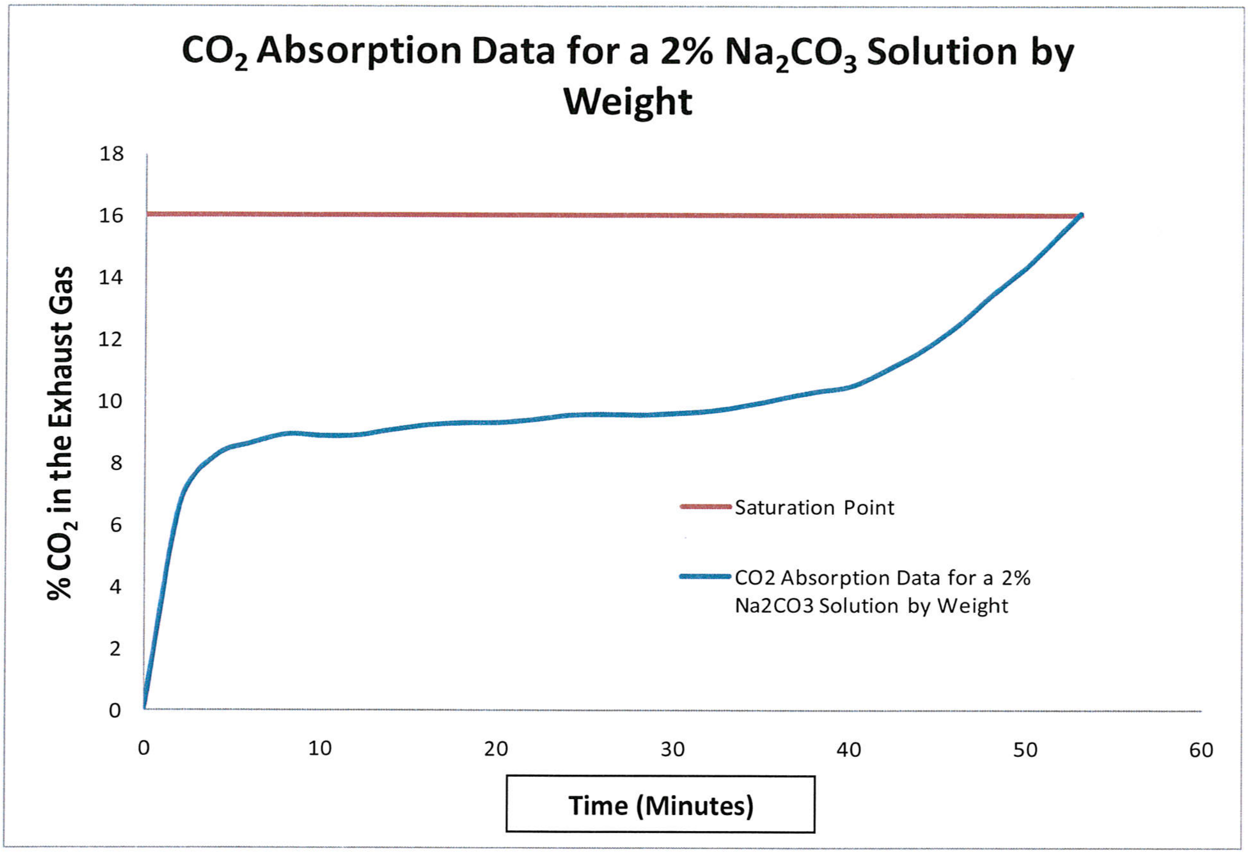


Figure 4: CO_2 absorption data for a 2% Na_2CO_3 solution by weight. 16.33 grams Na_2CO_3 in 800 grams distilled H_2O. 16% CO_2/balance air mixture in the gas feed stream (2.57 ml/sec CO_2 and 14.57 ml/sec air).

From observation of Figure 4 it can be seen that more than 50% of the CO_2 was absorbed within less than 5 minutes. It took about 50 minutes for the 2% Na_2CO_3 solution to fully saturate with CO_2.

Work Plan

Task 1: CO_2 Absorption in Alkaline Solutions

CO_2 absorption in several different alkaline solutions will be conducted at MTU. The experiments will be conducted at the bench scale level. The CO_2 absorption system can be seen below in figure 1.

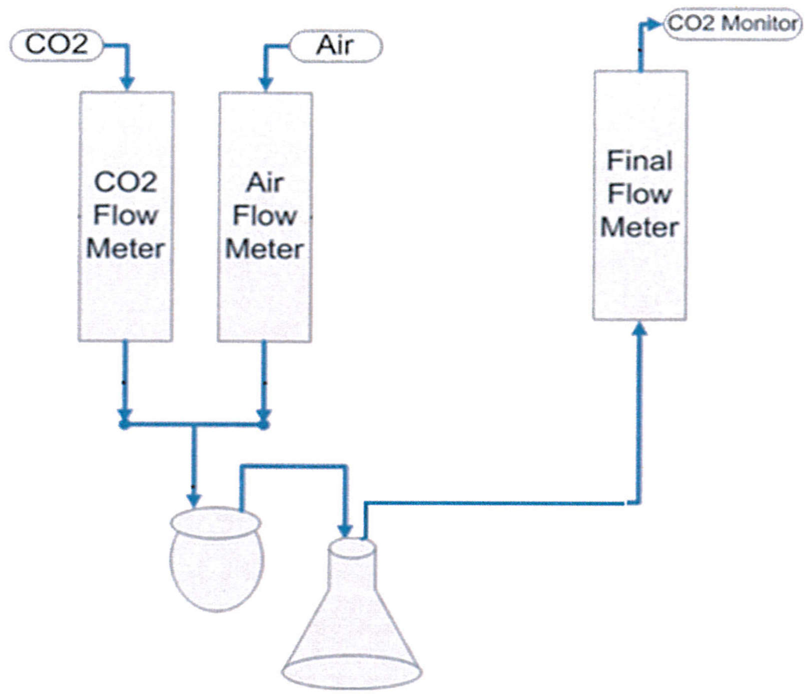


Figure 1: single flask bench scale scrubber system

The single flask scrubber system consists of:

- Two flow meters for monitoring the inlet gas flow of the CO_2 and air.
  - Industrial grade CO_2
  - Standard compressed air
- One 1000 ml Erlenmeyer flask to contain the CO_2 absorbent.
- A mixing chamber to promote uniform composition of the gas before it enters the Erlenmeyer flask.
- ASTM medium porosity gas diffuser to bubble the gas into the solution.
- Exit flow meter to monitor the exiting gas flow.
- CAI 600 Series gas analyzer to measure the $\%CO_2$ in the exiting gas stream.

The operating parameters of the system are:

- Room temperature
- Atmospheric Pressure
- 16% CO_2 in the gas feed stream
  - 2.57 ml/sec CO_2
  - 14.57 ml/sec Air

First, the Erlenmeyer flask is filled with a specific amount of alkaline solution. Gas is then fed, at the specified 16% CO_2, to the flask through a gas diffuser to allow the gas to bubble through the solution before exiting. The gas exiting the Erlenmeyer flask is fed to a gas analyzer that measures the % CO_2 in the exhaust gas. Results of the absorption experiments are plotted in graphical form as % CO_2 in the exhaust gas versus time. From these results it is possible to obtain the amount of CO_2 absorbed by the solution. The objective of these experiments is to identify the alkaline species that give the best CO_2 capture per unit cost, and to determine the optimum concentration of alkali.

Task 2: CO_2 Capture Studies using a Bicarbonate Solution

CO_2 absorption in an alkaline solution creates a bicarbonate solution as the product [1]. The reaction can be seen below in equation (1). The X in the term $X(CO_3)_{,s}$ refers to the alkali metal used to create the alkaline solution.

$$X(CO_3)_{(s)} + H_2O_{(l)} + CO_{2\,(g)} \rightarrow X(HCO_3)_{(aq)} \quad (1)$$

The solution is "saturated" with CO_2 when the amount of CO_2 in the feed stream equals the amount of CO_2 in the exiting gas stream. This indicates that the alkaline solution has been converted to a bicarbonate solution, and is no longer able to absorb CO_2. This CO_2-saturated liquid will then be reacted with a catalyst to produce CO_2 as a bi-product while regenerating the original bicarbonate solution.

To possibly increase CO_2 recovery, a 2nd stage scrubber unit will be fabricated and tested, with gases from 1st stage containing 8% CO_2 are passed through a Carbonate solution similar to stage 1. (See figure No.5)

Task 3: Preparation for Pilot Unit Studies

Carbontec Energy has previously sponsored a project at Michigan Tech, during which a unique laboratory-scale packed-column scrubber was fabricated. This scrubber was designed for processing custom mixes of gases with controlled temperature, pressure, and flowrate. A schematic of the current unit is shown in Figure 2. It is equipped with flow meters for all gases and liquids entering the scrubber. Outlet gases are passed to on-line instrumentation for continuously monitoring CO_2 levels. This unit will be used to establish the necessary process conditions for rapidly absorbing CO_2 and other pollutants using a specifically formulated sodium Carbonate solution. This unit has a capacity of approximately 5 cubic feet/minute, which is sufficiently high to simulate the performance of a larger-scale scrubbing unit. An initial version of this scrubber resulted in a CO_2 capture of 45%. An improved version increased the CO_2 capture to 55%. A second unit, similar to the first will be fabricated and installed in series with the first unit to determine if additional CO_2 can be captured. If this is successful, then a larger two stage unit can be considered in a future Phase II project (under a separate program) that would be installed and be placed in service at a North Dakota Power Plant. Further testing and the addition of this second scrubbing unit in series with the first at MTU are expected to improve the current capture of CO_2.

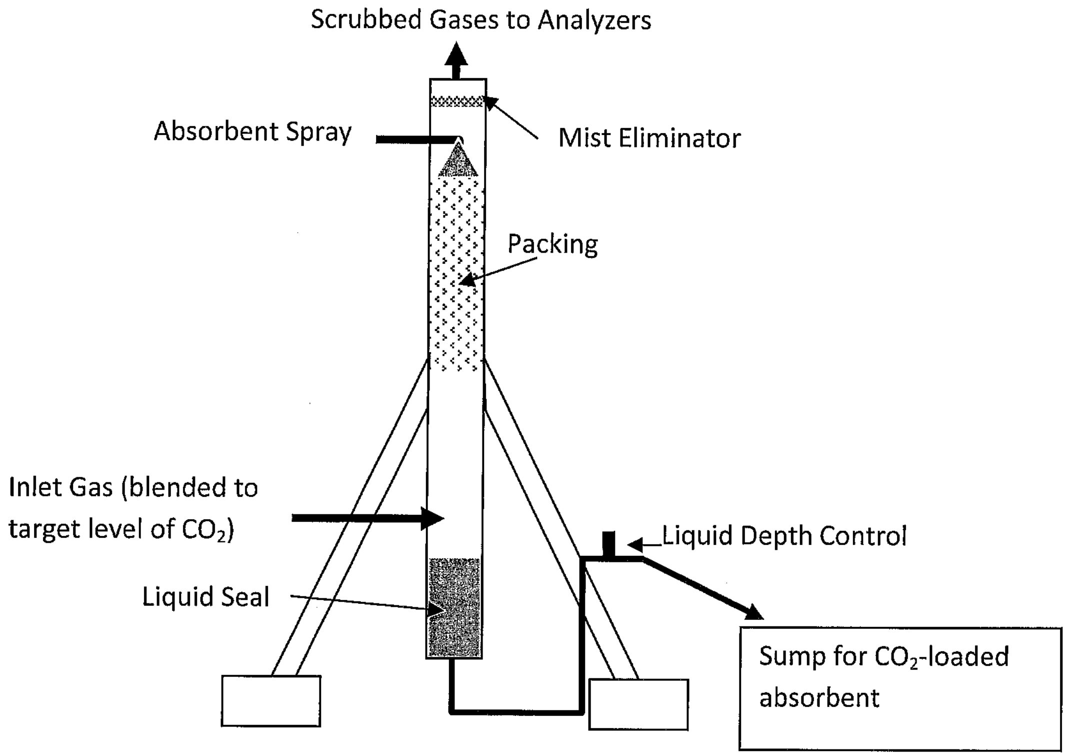


Figure 2: Schematic diagram of pilot-scale scrubber column. The column is 4 inches in diameter, and 9 feet high.

Task 4: MTU Studies

Bench scale tests will be conducted by MTU staff and a graduate student in the Chemical Engineering laboratories of Michigan Tech to obtain data required for the subsequent pilot plant studies. Once the second scrubber unit is fabricated, the 2 stage pilot scale columns and its associated support equipment will be set up, and tested to ensure that everything is functional. Personnel from MTU and Carbontec, will conduct the test work studies described in this Proposal.

Task 5: Analysis of on-site results

The results from the MTU studies will be analyzed to determine the performance that would be expected in a continuous operation at an actual plant. In particular, the necessary reaction volume for CO_2 sequestration, the appropriate column height and diameter, and the quantities of scrubbing agent for treating larger quantities of output gas from the plant will be reviewed.

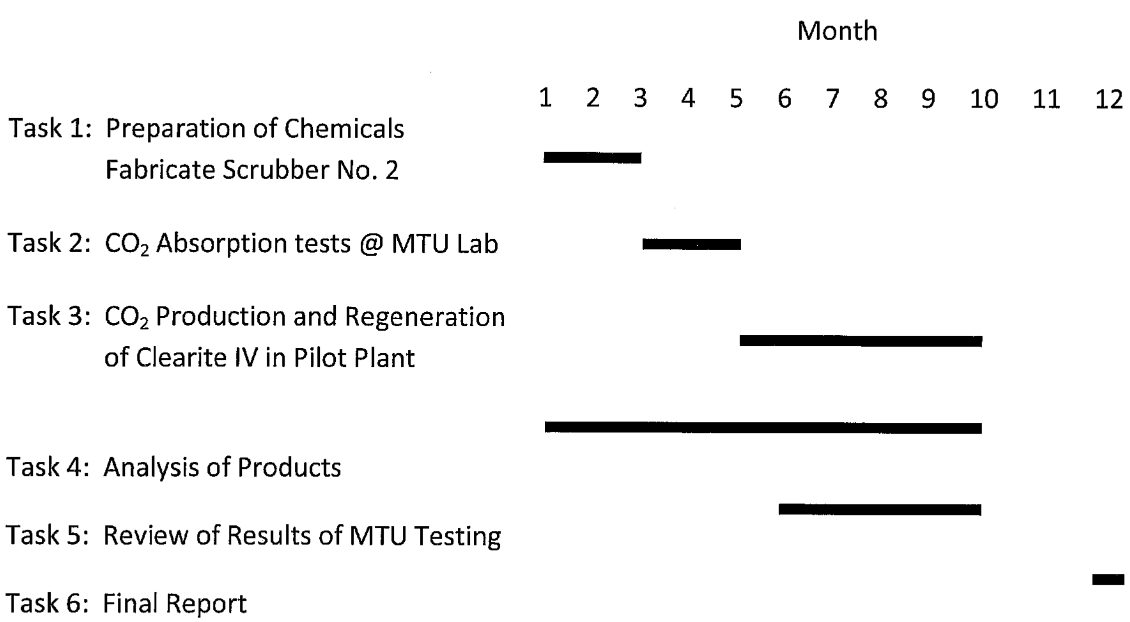
Deliverables

Deliverables will include data, interpretations, and conclusions of the various alkaline solutions tested for CO_2 absorption, and the results of the laboratory and pilot plant studies. The data will be presented as power point presentation at an interim meeting to monitor the progress of the work. A draft final report will be provided to the sponsors for review. After review of the draft, a final report will be written to conclude the project.

Timeline

The project is expected to take 12 months to complete, with an estimated timetable for each task shown in Figure 3:

Figure 3: Estimated Project Timetable



Standards of Success

The success of this project will be based on the effectiveness of the alkaline Carbonite (Clearite VI™) solution to capture CO_2 from simulated power plant emissions. This will be determined through a series of experiments and analysis outlined above in the work plan section.

The success will also be based on the second objective, the potential to process the CO_2 saturated alkaline carbonate solution with a catalyst that will provide for the regeneration of the original bicarbonate capture solution while releasing the captured CO_2 as a marketable product.

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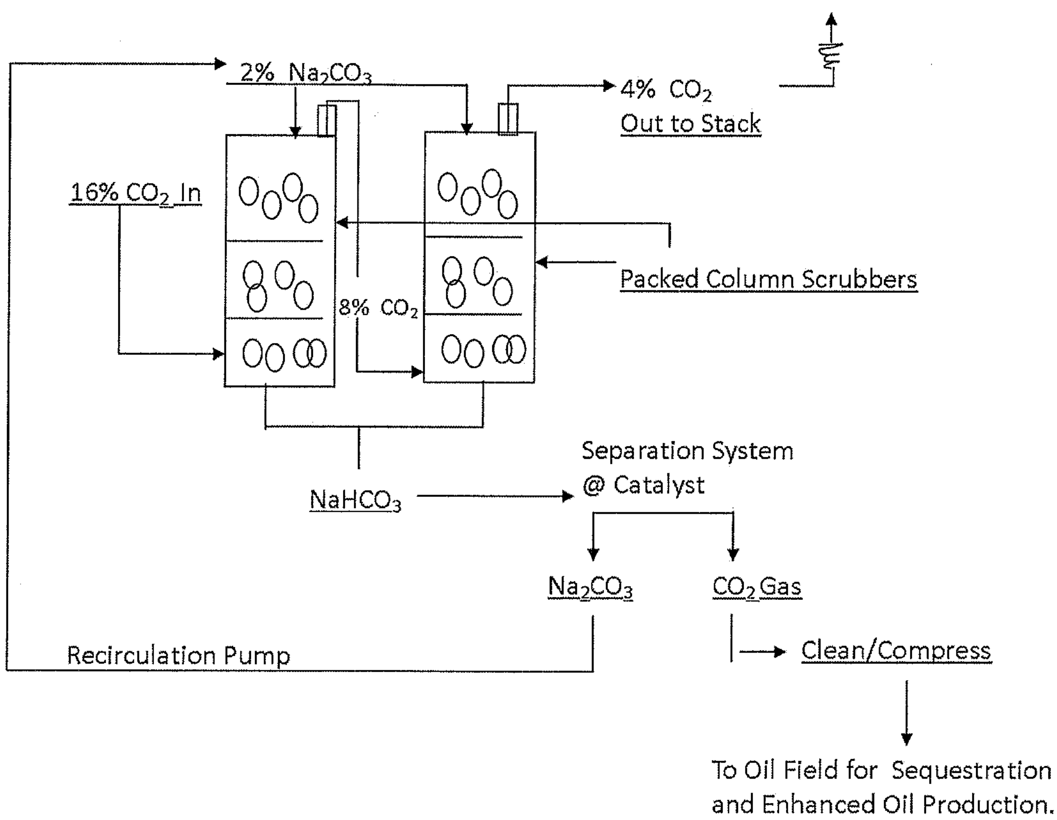
Chemical Engineering Department

Figure 5

MTU/ CEC 2 Stage CO_2 Capture /Sequestration Process
Production of CO_2 for Oil Production Enhancement



Pilot Scale Capture of Carbon Dioxide from Flue Gases

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Michigan Tech — Create the Future

Introduction

Increasing concerns over global climate change have led to concern over the capture of CO_2 from industrial flue gases. This impetus has led Michigan Technological University (MTU) to develop a pilot scale CO_2 wet scrubber to capture the CO_2 emitted from flue gases. This is currently the only wet scrubber for CO_2 absorption in the world.

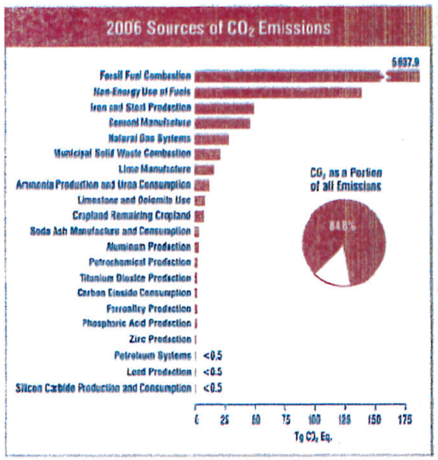

Figure 1: 2006 Sources of CO_2 Emissions [1]

As can be seen from figure 1 above, fossil fuel combustion and iron and steel production account for the majority of CO_2 emissions. The research at MTU is aimed at reducing emissions in these two areas.

OBJECTIVES

•The majority of power plants that burn fossil fuels have a similar wet scrubber in place for removing sulfur dioxide (SO_2). The goal is to develop a technology that can utilize current SO_2 wet scrubbers to absorb SO_2 and CO_2 simultaneously.

•Evaluate the effectiveness of different absorbents using the wet scrubber.

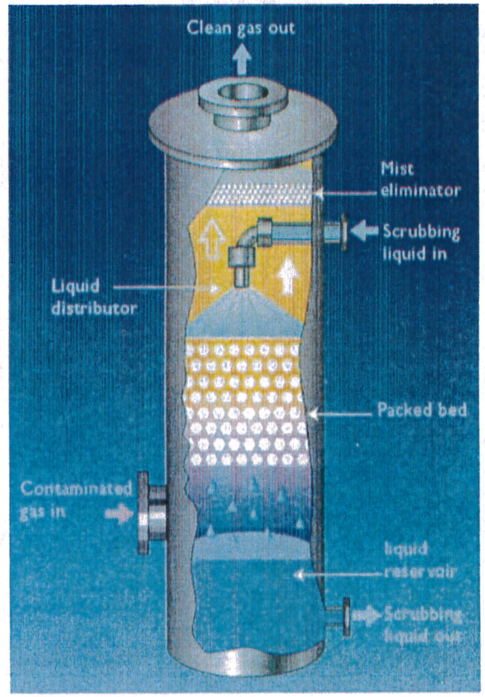

Figure 2: Diagram of a Wet Scrubber [2]

BACKGROUND

The basic principle of an absorption column is mass transfer with a reaction. The absorbent is pumped in through a spray nozzle near the top of the column while the CO_2 rich gas is fed from an inlet near the base of the column. This creates a countercurrent flow between the gas and the absorbent. To increase contact between CO_2 and the absorbent a packing material is added to the column. This part of the column is commonly referred to as the packed bed and it is where most of the absorption of the CO_2 takes place. The mist eliminator is in place to remove any liquid that may be entrained in the vapor [3].

PRELIMINARY RESULTS

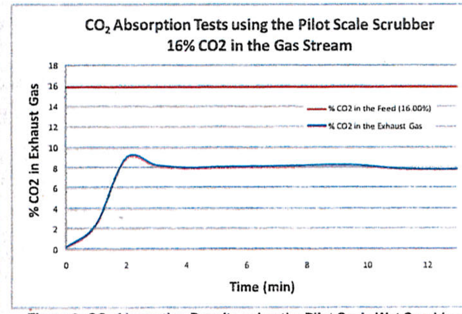

Figure 3: CO_2 Absorption Results using the Pilot Scale Wet Scrubber

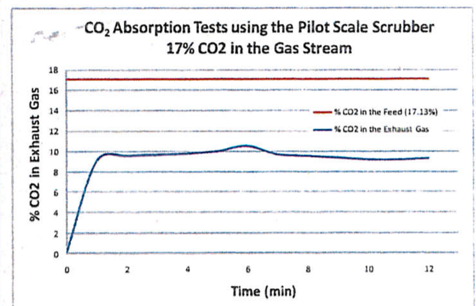

Figure 4: CO_2 Absorption Results using the Pilot Scale Wet Scrubber

CONCLUSIONS

• The preliminary results show that the absorbent currently being tested can continuously absorb 50% of CO_2 in a gas stream that is fed to the wet scrubber. As can be seen from figure 1, this would reduce CO_2 emissions from fossil fuels alone, by 2,819 teragrams of CO_2 equivalent. This proves that the absorbent being tested can be used with a wet scrubber technology.

References

1)"Global Greenhouse Gas Data | Climate Change - Greenhouse Gas Emissions | U.S. EPA." *U.S. Environmental Protection Agency*. Web. 15 Feb. 2010. <http://www.epa.gov/climatechange/emissions/globalghg.html>.

2) "Croll Reynolds Air Pollution Control Systems - Products." *Croll-Reynolds - A Global Leader In Custom Engineered Process Vacumn, Jet Ejector, Power and Air Pollution Control Systems*. Web. 15 Mar. 2010. http://www.croll.com/_website/ca/products.asp#ws

3) *Steam: Its Generation and Use*. [Whitefish, Mont.]: Kessinger, 2006.

CEC/MTU CO_2 CAPTURE/SEQUESTRATION

NORTH DAKOTA PILOT PLANT PROJECT BUDGET

CEC/MTU CO_2 Capture/Sequestration

North Dakota Pilot Plant Project Budget

Phase I

Laboratory

Bench Scale Testing, MTU Staff and Graduate Student	$ 19,700
Fabrication of 2nd Stage Scrubber, Pilot Scrubber Tests, MTU Staff, Graduate Student, Carbontec Staff	47,000
Travel	6,900
Materials/Supplies	3,800
Laboratory Services, Supplies, General Overhead, Accounting, Preparation of Report	18,600
Sub-Total:	$ 96,000
TOTAL BUDGET:	**$ 96,000**

	%	Amount
North Dakota Industrial Commission Share	**50.0**	**$48,000**
Project Commercial Sponsors	**50.0**	**$48,000**
Total:	**100.0**	**$96,000**

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May 6, 2016

Ms. Karlene Fine
Executive Director
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kfine@nd.gov

Re: Proposal dated April 1, 2015 entitled "Capture and Sequestration of Carbon Dioxide"

Dear Ms. Fine:

We have reviewed the Lignite Energy Research Policy related to public information and patents.

We are in agreement with the provisions of 43-03-06-01 and 43-03-06-03, use for governmental purposes.

However, we request a waiver as provided under 433-03-06-03 based on:

1. We will request a waiver from those companies that will provide the matching funds, a waiver of their requirements that conflict or may conflict with this section.
2. Other sources will fund more than twenty percent of the projects funding.
3. It is unlikely the State would ever seek to use the right given to the State under this section.

We trust that the Council and commission will see to act favorably and approve our proposal.

We are ready to proceed with the project once the appropriate agreement is in place and the Notice to Proceed is issued.

Regards and Best Wishes,
Yours Very Truly,

John Simmons
Chairman
Carbontec Energy Corporation