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Subtopic: **d. Monitoring of CO2 Geologic Storage**

Title: Subsurface Monitor for Dissolved Inorganic Carbon at Geological Sequestration Site

SHEETA Global Technology Corporation

Phase I SBIR Final Report

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Executive Summary

Statement of problems addressed

Phase I research of this SBIR contract has yielded anticipated results and enable us to develop a practical new instrument to measure the Dissolved Inorganic Carbons (DIC) as well as Supercritical (SC) CO_2 in underground brine water at *higher sensitivity, lower cost, higher frequency and longer period of time* for the Monitoring, Verification & Accounting (MVA) of CO_2 sequestration as well as Enhanced Oil Recovery (EOR). We show that reduced cost and improved performance are possible; both future and emerging market exist for the proposed new instrument.

What's done in phase I

Besides accomplishing the proposed objectives and tasks in phase I proposal, we also had an invention that enable us to make the final system at lower cost, better performance. We also discovered new functionality for our system, i.e. to measure SC CO_2.

Commercial Applications and other benefits

The proposed research will provide a powerful tool for sub-surface MVA and EOR of CO_2 at sequestration sites, including low production oil fields. The technology will also find great market opportunities in industrial process control, medical care and other researches. The final instrument will have great impacts for the ultimate accurate MVA of sequestrated CO_2, creating green energy jobs in support of the Recovery Act, and improve the security of domestic energy supply through Enhanced Oil Recovery.

Key words

Sub-surface MVA CO_2 Geological Sequestration Site, Enhanced Oil Recovery and CO_2 sequestration, Quantum Cascade Laser Spectrometer

Summary for Members of Congress

The proposed research project will develop the competitive technology for US leadership in the MVA of CO_2 at geological sequestration site, creating green energy jobs, and improve national Energy security.

Title: Subsurface Monitor for Dissolved Inorganic Carbon at Geological Sequestration Site

1. Identification & Significance of the Problem & Opportunity

Proposed Project Represents an Important Advancement for DOE Goals

During future CO_2 geological sequestration, millions tons of supercritical CO_2 will be injected into underground brine reservoirs, the injected CO_2 will be dissolved in brine and incorporated into minerals. Reliable and cost-effective monitoring, verification, and accounting (MVA) of the CO_2 in these locations will be an important part of implementing Carbon Sequestration[1]. The MVA process includes tracking the location of the injected CO_2 plume, ensuring that the injected CO_2 is not leaking, and verifying the quantity of CO_2 that has been injected underground, dissolved and sequestrated. DOE is looking for the "Development of Novel, Robust Sensing Approaches for CO_2 Storage Injection and Monitoring in Deep Sub-Surface Environments" (DE-FOA-0000732). Technologies need to provide information of the *CO_2 plume and pressure front*, monitor the condition and performances of the injection well. The sensor technologies must be able to provide long term operation under harsh borehole and subsurface conditions, i.e. high temperature (up to 250 C with depths ranging from 2,500 to 12,000 ft), high pressure (up to 10,000 psi, generally, but dependent upon injection formation and injection permit), corrosive liquids (e.g. dissolved and liquefied CO_2 with trace Nitrous Oxides and Sulfur Oxides with pH near 4), and high salinity (up to 250,000 ppm).

As the injected CO_2 plume advances in underground aquifers, the plume will bring huge changes in CO_2 species, i.e. Supercritical CO_2($SCCO_2$), carbonic acid, dissolved carbonate and bicarbonate species. As $SCCO_2$ and other species are all miscible or dissolvable with water, here we categorized all of them, including $SCCO_2$, as Dissolved Inorganic Carbons (DICs). Therefore, the knowledge of (DIC), i.e. concentration, formation and extent will be the key of MVA.

Not just limited for MVA of the proposed large scale CCS operations, we also have explored and discovered that there is potential existing market for monitoring underground DIC and SC CO_2 during the Simultaneous Water Alternating Gas (SWAG) injection for the purpose of Enhanced Oil Recovery (EOR) during which CCS also naturally happens as a free gift to EOR. CO_2 based SWAG for EOR is considered as a potential way for revitalizing existing low production oil fields where economical amount of natural CO_2 is readily available, and in the near future one of the vital incentives for CCS is EOR. Right now, characterization of the SWAG injection is only conducted at the wellhead, and underground DIC and SC CO_2 data of the 3-phase fluid are very important for us to understand and feedback control of the SWAG injection, and thus improve oil recovery and save CO_2 injected. The detailed market analysis is given in the Commercialization Plan section. Therefore, both CO_2 based SWAG for EOR and MVA for CCS require the same instruments that could characterize underground DIC and SC CO_2 in real time and at relatively low cost.

Therefore, this proposal addresses the needs to measure the DIC as well as SC CO_2 in underground brine water at *higher sensitivity, lower cost, in situ, at higher frequency and over long period of time* for the Monitoring, Verification and Accounting (MVA) of CO_2 sequestration, as well as CCS process coupled with Enhanced Oil Recovery (EOR). The current manometer type of technology for measuring DIC as well as 3-D seismic imaging of SC CO_2 pockets in reservoirs, are discussed along with the proposed Mid-IR spectroscopic measurement method using Quantum Cascade Lasers (QCL). We propose that QCL based spectrometer could provide higher sensitivity of DIC and SC CO_2 measurement at lower cost and higher frequency, and therefore could quantify and resolve at high sensitivity over an extended region or spatial scale; improve the reliability of next-generation detection and sensing technologies; and quantify the mass of sequestered CO_2, not only over its volume (both depth and lateral extent) but also as a function of time because our proposed instrument will be able to operate sub-surface at the bore-hole over a long period of time. The phase I research has successfully built the *proof of principle* prototype QCL based spectrometer for underground brine CO_2 sequestration MVA. We will leverage phase I results along with our past demonstrated results on QCL laser technology and Mid-IR spectroscopy and our collaborative research on molecular simulation to predict the Mid-IR spectra for DICs and SC CO_2 as the pressure, pH, temperature and salinity change, thus validating and guiding the prototype product to be built in phase II of the project, which could be applied in the field for measuring DIC and SC CO_2 for MVA and EOR purposes.

Measuring DIC in water and implications for MVA of CO_2 underground brine sequestration

Background on Dissolved Inorganic Carbon (DIC)

Dissolved/Total Inorganic Carbon (DIC/TIC) includes 4 forms of dissolved CO_2, i.e. CO_2 (aq), H_2CO_3, HCO_3-, and CO_3^{2-}. They distribute in water according to following balances along with CO_2 in the gas formation (CO_2(g)).

- CO_2 is a simple gas which Henry's law applies for the equilibrium between vapor and liquid:

$p_{CO2} = K_H\ CO_2\ (aq)$ for the balance of $CO_2\ (g) \Leftrightarrow CO_2\ (aq)$

Where p_{CO2} is the partial pressure of the gas in the bulk atmosphere (Pa), K_H is constant (Pa) and CO_2 (aq) is the equilibrium mole fraction of solute in liquid phase. With 400ppm of CO_2 in the air the dissolved CO_2 is 1.2×10^{-5} mole/l or 0.5mg/l at 25° C.

- Equilibrium is established between the dissolved CO_2 and H_2CO_3, carbonic acid.

$CO_2\ (aq) + H_2O \Leftrightarrow H_2CO_3\ (l)$, with equilibrium constant $K_r = \frac{[H_2CO_3]}{[CO_2]aq} \approx 1.7.10^{-3}$

At equilibrium, only a small fraction (ca. 0.2 - 1%) of the dissolved CO_2 is actually converted to H_2CO_3. But we still write CO_2 (aq) by convention as H_2CO_3. In fact, the pK_a most reported for carbonic acid ($pK_{a1} = 6.37$) is not really the true pK_a of carbonic acid. Rather, it is the pK_a of the equilibrium mixture of CO_2 (aq) and carbonic acid.

- Carbonic acid dissociates in two steps.

$H_2CO_3 + H_2O \Leftrightarrow H_3O^+ + HCO_3^-$ pK_{a1} (25 °C) = 6.37

$HCO_3^- + H_2O \Leftrightarrow H_3O^+ + CO_3^{2-}$ pK_{a2} (25 °C) = 10.25

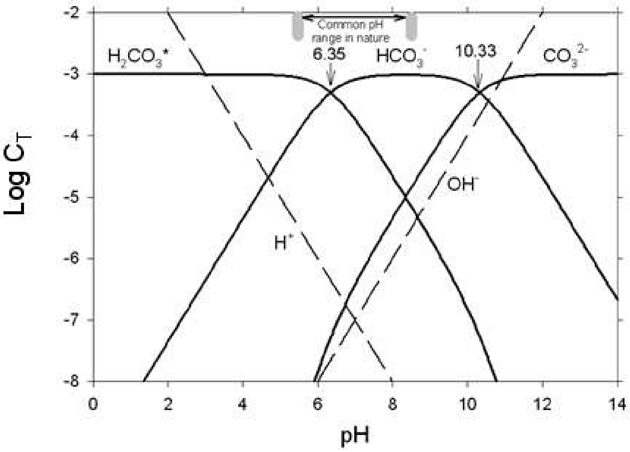


Figure 1. DIC species distribution versus pH

Depending on pH and temperature, the DIC will disassociate into varying amount of the carbonate species H_2CO_3 (CO_2 (aq)), HCO_3^- and CO_3^{2-}, as shown in the figure on the right. As the [CO_2(g)] increases, e.g. a CO2 injection happens in underground water reservoir, then the [CO_2 (aq)] increases proportionally, and so does the DIC/TIC. So, if we could ***measure one of the forms of DIC, e.g. the [CO_2 (aq)], and pH,*** i.e. [H^+] accurately, ***along with temperature and pressure***, then ***we could determine the DIC in all forms. From the figure on the left, it is obvious that at different pH, we should measure different species in order to maximize the accuracy in DIC. For pH<6.35, CO_2(aq) is the best candidate; and for 6.35<pH<10.33, it is best to measure HCO_3^-; in the rare case of very basic water, i.e. pH>10.33, it is best to measure CO_3^{2-}.***

Implications of measuring DIC in water for MVA of carbon seqestration

For CO_2 sequestration project, where large amount of CO_2 injected into underground brine water body will need to be monitored, verified and accounted, we need online measurements of DIC in brine water deep underground to help the following tasks,

1. Deep monitoring of brine (*deep underground water*) storage formation at distance from injection:

a. Define area of influence. How far does the plume reach? This could be used in legal disputes over ownership of pore space.

b. Define the amount of dissolved CO2 or measure DIC. SC CO_2 is immiscible with brine and right now we really do not know how to measure any dissolved phase. The basic question "how much dissolves?" is fundamental to our understanding of geochemical sequestration processes in the reservoir. If this tool could somehow help us to do so, it would be a huge advancement in our basic science understanding and to our understanding of geochemical processes in a sequestration reservoir.

2. Shallow monitoring of non-saline groundwater --- we need a cost effective way to monitor portable aquifers above sequestration sites for any changes that might signal a leak that may threaten ground water resources.

3. Monitoring near abandoned wells and faults. These are sites thought to be the most plausible for leakage because they are preferential pathways of migration that cut through sealing shale layers.

In-situ Characterizing SC CO_2

As pointed out by Review #3 of our phase I proposal, we also recognize that SC CO_2 is the other most important form of the injected CO_2 during geological sequestration. As SC CO_2 always forms when pressure is over 73 bar and 31.1°C (figure one the right), so SC CO_2 will be the dominant form when freshly injected underground. *SC CO_2 is immiscible with water*, although there is still equilibrium between SC CO_2 and brine, the total amount of SC CO_2 cannot be characterized by DIC measurement only. After careful study of SC CO_2 in the underground conditions, we believe that our underground DIC instrument could also monitor the existence of SC CO_2 with minimal modification. This capability will be very important for the more complete MVA of CCS, and it will also enable new applications in SC CO_2 Enhanced Oil Recovery and CCS as we discuss below.

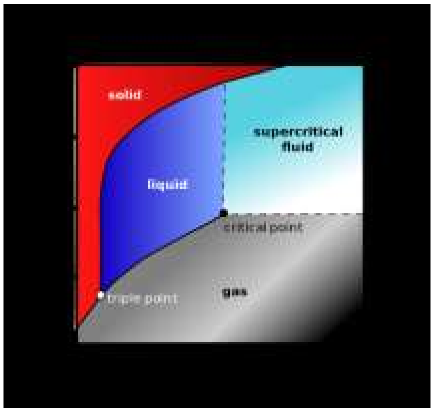


Figure 2. CO2 phase diagram

2. Significant Benefits of Proposed Instrument versus Current Technology

Huge gap between current available technology and need for MVA of CO2 sequestration

The current technology used by geologists for DIC measurement is menometer. The method first uses acid to titrate the brine water with pH>6, and therefore majority of the dissolved CO2 are in the form of $[HCO_3^-]$ and $[CO_3^{-2}]$. When the pH reaches 4 after titration, the amount of acid titrated will give the total amount of $[HCO_3^-]$ and $[CO_3^{-2}]$, and the total CO_2 dissolved or DIC is roughly measured.

During a measuring cycle a sample is drawn from the subsurface bore hole and its volume is expanded in a measuring chamber. Due to the volume expansion a gas phase is generated in the measuring chamber. To accelerate equilibration of pressure and temperature between the liquid and gas phase, the sample is stirred with an impeller. In some measuring systems the equilibrium pressure is not reached within an acceptable time and must therefore be extrapolated. The CO_2 content is then calculated from the measured equilibrium pressure and temperature. This measuring principle is inherently not selective for CO_2 as all other gases dissolved in the sample will also influence the gas pressure and thus cause interferences. A selective method for CO_2 determination would be of special interest in situations where in addition to CO_2 other gases are also contained in the liquid. *Obviously, the current process requires the measurement to take the samples out from the high pressure and high temperature underground water reservoir with U-tubes --- like the aluminum cans that hold carbonated drinks, and measurements are therefore both time and money consuming.*

A literature survey for alternative methods for CO_2 determination reveals other approaches as well. These are capillary-type isotachophoresis[2], the use of a modified gas analyzer[3], flow injection analysis systems[4, 5], the use of a gas electrode with an air gap, and a pH meter. While being interesting from a scientific point of view, these methods lack robustness and simplicity, which hinders their application in underground brine sequestration MVA. A selective, direct spectroscopic method that could be deployed underground is therefore of considerable practical interest for MVA of CO2 sequestration.

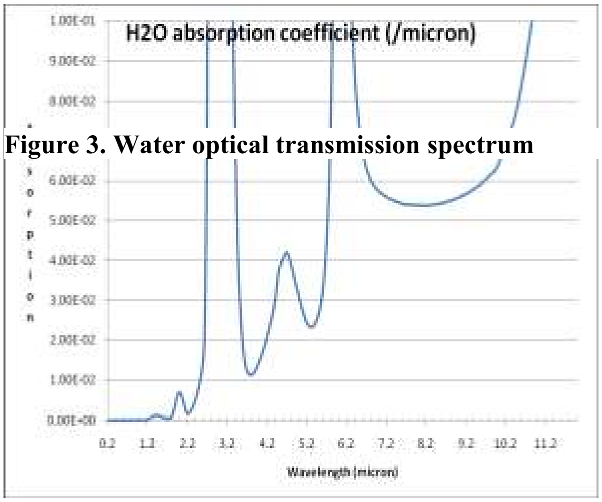


Figure 3. Water optical transmission spectrum

Water's limited transparent window in the Mid-IR and the proposed new method

For water, the "limited transparent" windows in the Mid-IR[6] are the 3.5~5.5μm and the 6.5~10μm regions (see figure on the left side). The absorption coefficient α is about 120/cm to 420/cm at the 3.5~5.5μm region; and about 550/cm to 650/cm at the 6.5~10μm region. The chemicals in trace amount dissolved in water should have strong absorption in these 2 windows in order to be detected in the Mid-IR.

CO_2 dissolved in water gives rise to a strong and characteristic absorption band at 2,342cm^{-1} (Fig. 4 from Reference[7] on the right side). From figure 4, the inferred absorption coefficient is ~6/mm for 1.35g/L, or ~600ppm dissolved CO_2. Apart from water practically no other substances that are usually present in CO_2-containing liquids exhibit absorption bands in this spectral region. This offers the opportunity to develop a simple and selective analytical method for CO_2 determination in aqueous solutions based on mid-infrared (MIR) absorption spectroscopy. Because of the low frequency of this fundamental vibration, its overtone bands cannot, at present, be measured with the required sensitivity in the near-infrared spectral region. A difficulty in measuring the fundamental CO_2 vibration for process analytical applications is the strong absorption of water at 2,342 cm^{-1}, which restricts the optical path for transmission measurements to a few micrometers when using conventional thermal light sources, i.e. FTIR. A way out of these problems would be the use of a dedicated, powerful light source that allows transmission measurements at extended optical paths (>100 μm). Only recently, room-temperature quantum cascade lasers (QCL) have become available that provide an average CW output power of 1W or more[8] and able to work at well over

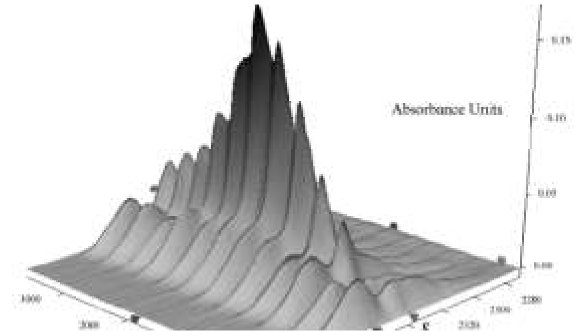


Figure 4. Mid-IR spectrum of CO2 dissolved in water at 4.3micron

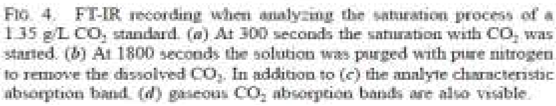


FIG. 4. FT-IR recording when analyzing the saturation process of a 1.35 g/L CO_2 standard. (*a*) At 300 seconds the saturation with CO_2 was started. (*b*) At 1800 seconds the solution was purged with pure nitrogen to remove the dissolved CO_2. In addition to (*c*) the analyte characteristic absorption band, (*d*) gaseous CO_2 absorption bands are also visible.

100°C[9]. They could extend the measurement optical paths to over 100s µm as we argued below in the limited transmission windows of water.

Using a Thermo-Electric (TE) cooled MCT detector with peak detectivity at 4.3µm, we have a detectivity D* of ≥8x10^{9}cmH$^{1/2}$/W, and therefore with a 0.01mm diameter detector and pulsing the QCL at 1kHz with 100µsec pulses (10kHz bandwidth), we should have a NEP of 1.25x10^{-12} W. If we could achieve peak power of 1W, then we should have a loss budget over 10^9 with a signal to noise ratio of >100 over 1 sec averages. Therefore, the optical path should be able to reach as long as 0.6mm, or an attenuation of OD 13.5 based on the absorption coefficient α~22/mm.

By using a small area (0.1mm diameter) detector, QCL has demonstrated an extended absorption path length inside water, i.e. 130µm, versus FTIR's 30µm at a wavelength of 4.3µm[10]. This past result could be further improved with latest higher peak power pulsed QCL, i.e. >10W versus the 50mW power, and also using more sensitive detectors tuned for 4 micron detection instead of their detector which is responsive up to 12µm but has a detectivity about 2 orders of magnitude lower. In principle, we could focus the QCL beam into a 10x10µm area without much problem. With all these improvements, the penetration depth to well over 500µm is possible at 4.3µm, and even to >1mm at the wavelength of 3.8µm, i.e. water's absorption minimum point.

Current technologies for in-situ monitoring underground SC CO_2

The currently available technologies for in-situ monitoring underground SC CO_2 are quite limited. Seismic imaging is considered as a viable method, as the SC CO_2 will change the density of the seismic layers that SC CO_2 reaches. But, the measurement can not 100% positive that the change of density is a result of SC CO_2 invasion, a direct measurement of SC CO_2 existence is still highly desirable.

We found that SC CO_2 actually has similar Mid-IR absorption feature as dissolved CO_2 in water, i.e. SC CO_2 also shows a sharp feature at 2,348cm^{-1}, almost the same location as CO_2 dissolved in water, with the exception of the co-existence of the shifted and broadened P and R branch which doesn't exist in CO_2 dissolved in water[11], see figures below.

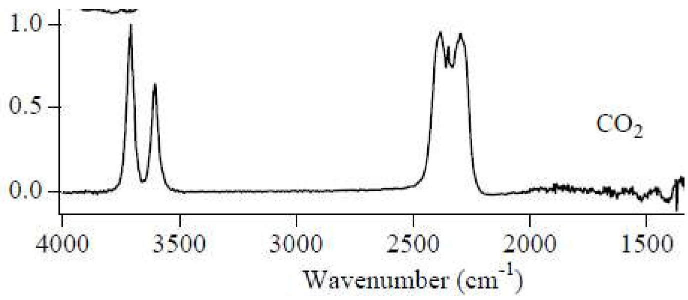
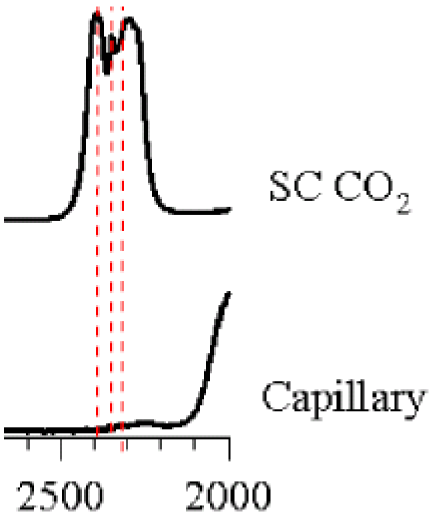


Figure 5 (top and right[11]). Mid-IR spectra of SC CO2 in a capillary of 115µm ID. The sharp feature at ~2,340cm-1 is quite obvious, along



with the P and R branch of the CO2 gas phase spectra, maybe broadened and shifted.

This means that our proposed instrument could be used for the measurement of the existence of SC CO_2 as well. This instrument could easily distinguish between dissolved CO_2 and SC CO_2 underground. A detailed molecular spectroscopy simulation is underway (our collaboration with Caltech's Brine Mid-IR spectroscopy simulation project, funded by DOE DE-FE0002057) for the quantitative measurement of SC CO_2 under high pressure and relatively high temperature (50~100°C) conditions.

Past Reference Experimental Data

Table 1. Past reports of QCL probing water optical path lengths and the detection limits.

Optical pathlength	Wavelength	Comment: Detection limit
~ 120µm[7, 12]	4.34µm	CO2 Standard deviation 11.3mg/l, detection limit 33.9mg/l
580µm[13]	5.4µm	An absorption coefficient of 0.023/µm is measured

From the maximum absorption pathlength of 580µm demonstrated at 5.4µm[13], we believe it is reasonable to have a similar path length at 4.34µm (2,340cm^{-1}) where the absorption is calibrated to be ~ 0.024/µm. In reference [13] where work was done before 2004 and 580µm of pathlength is demonstrated, they used a weak laser with peak power less than 2mW and duty cycle of 1.5%, or average power only 30µW.

3. Phase I results --- Degree to which Phase I has Demonstrated Technical Feasibility

We have accomplished all the tasks and objectives in our phase I proposal as listed below. We also have an invention that makes this technology more cost-effective, and with the promise to add new capability to our proposed instrument, i.e. underground measurement of SC CO_2.

Proposed Phase I tasks and objectives

The following are the *objectives* in our phase I proposal.

- Demonstrate and validate Reference/Normalization scheme for pulsed QCL measurement in water, demonstrating improved signal to noise ratio.
- Use of two QC lasers at widely spaced wavelengths to demonstrate improved ability to subtract baseline drift effects.
- With the results above and discussion with regional sequestration research team, propose and design the prototype for phase II.

Phase I of the proposed project should met to two technical *milestones* that we propose to achieve

Milestone 1. By the end of month 6, Complete setup of the dual wavelength and dual detector system.

Milestone 2. By the end of moth 8, Demonstrate that the ultimate sensitivity and ability to deduct matrix caused background drift.

The following are the task items for our phase I proposal,

Task I. Setup and Conduct dual wavelength QC laser measurement with normalization

Subtask 1. Build dual wavelength QC laser system at desired wavelengths and combine them into HW.

Subtask 2. Build dual Signal/Reference detector system and combine them with control and DAQ PC system.

Subtask 3. Build the titration water sample flow so we could control the pH and the concentration of CO2(aq) in the water sample.

Subtask 4. Take data and change software to validate the normalization and removal of matrix effect.

Task II. Design and budgeting for the prototype in phase II.

Subtask 1. Preliminary design and budgeting the phase II prototype.

Using the results from task I, we will have an idea about the ultimate sensitivity achievable with QC lasers currently commercially available. We will give preliminary design and budget for the phase II prototype. The design will take into consideration the following factors with top priority first:

- The rugged, compact nature of the final system that could be deployed at well bore-holes
- The cost and budget for developing the final system

Subtask 2. Locating field test partners with potential regional partnerships for phase II

Experimental setup

As we proposed in phase I, we built the prototype QCL spectrometer with Absorption over Reference Normalization capability. Two detectors are used --- first one as the Reference signal before the water sample and the second one as the Absorption signal after the water sample. The ratio of two signals are processed in real time, i.e. Normalization, and we achieved the following results.

We also experimented the detection limit for CO2 dissolved in water, and the measurements were carried out both with dual pulsed QCL scheme and a single CW modulated widely tunable QCL scheme --- details are given below.

Demonstrated usable pathlength and improved signal to noise ratio through Normalization scheme

In phase I research, with latest current commercial QCLs, we could achieve peak power well over 400mW at duty cycle of 2% and pulse width of 50nsec, and demonstrated over 400μm of usable pathlength, i.e. with a pulse signal over noise of 10 to 1 (500 pulses averaged in 1 second) after penetration of 400μm of water sample at 4.3μm. Here we used detector operating under room temperature without TEC cooling (VIGO PVI5), which has a detection limit 20 times higher (or poorer) than a cryogenic cooled detector. The use of uncooled detector is desirable for underground operation because of limited cooling capability and power supply, even though we compromise on the usable pathlength. The 400µm pathlength is achieved without Signal/Absorption real time Normalization scheme, and an extra 30~50µm usable pathlength is achieved when we applied the Reference/Absorption scheme.

We also attempted fast ramping of QCL at low duty cycle over 100µsec period instead of pulses at 50nsec. Here, the usable power is about 20mW to 80mW at the peak, and we achieved usable pathlength of 320µm after some 100 averages in one seconds, again an extra 40~50µm usable pathlength is achieved when we applied the real time Normalization of Reference/Absorption scheme.

The results of the usable pathlength demonstrated with two QCLs modulated at different schemes are presented in the table below.

Table 2. Usable pathlengths using two QCLs at different modulation schemes.

Modulation scheme/ QC laser used	Usable Pathlength w/o Normalization scheme	Usable Pathlength w/ Normalization scheme	Peak / average power to the sample
50nsec 2% Pulsed	400µm	430~450µm	300mW
100µsec modulation	320µm	360~370µm	80mW/50mW

Demonstrated wavelength scanning that remove background

Because our newly invented modulation scheme could let us use only 1 QCL for the wavelength scanning and then removal of shifting background, we tested both the proposed "dual wavelength that remove background" ("Dual wavelength") and the "scanning wavelength that remove background" ("Scanning Wavelength"). The "Dual Wavelength" scheme uses two fixed wavelength spaced about 40cm-1 apart, while the "Scanning Wavelength" uses 1 QCL modulated over 16cm^{-1}. We achieved background removal when tested without any CO_2 present in water, and get a fluctuation of δ=0.00012M (or ~5mg/L of CO_2 in water, calibrated with 0.01M of CO2 generated in water by acidification of 0.01M of $NaHCO_3$) over 1 hour period with "Dual Wavelength" and normalization scheme; while δ=0.00005M (or ~2.2mg/L of CO2 in water) over 1 hour period with "Scanning Wavelength" and normalization scheme. Our CO_2 sample cell right now cannot maintain accurate concentration of CO_2 dissolved over long period of time, and therefore we did not test the fluctuation for elevated amount of CO_2, but expect to get numbers very close to the zero CO_2 measurement.

We also conducted measurements with solution other than NaHCO3, such as glucose and sugar, where the baselines will be shifted compared to pure NaHCO3 solutions. We also got same reading of CO2 concentration, indicating that matrix effect is removed[12].

Since the "Scanning wavelength" scheme represents much better signal to noise ratio, we conducted a series of measurement of CO_2 dissolved in water with the "Scanning wavelength" scheme and presented the results in the plot below. We could see that without Reference/Absorption Normalization, the noise is very obvious, and at zero CO_2 concentration, the noise level is about ~20 times stronger for the scheme without Normalization versus the scheme with Normalization. Here, the results are averaged 100 times over 1 second period.

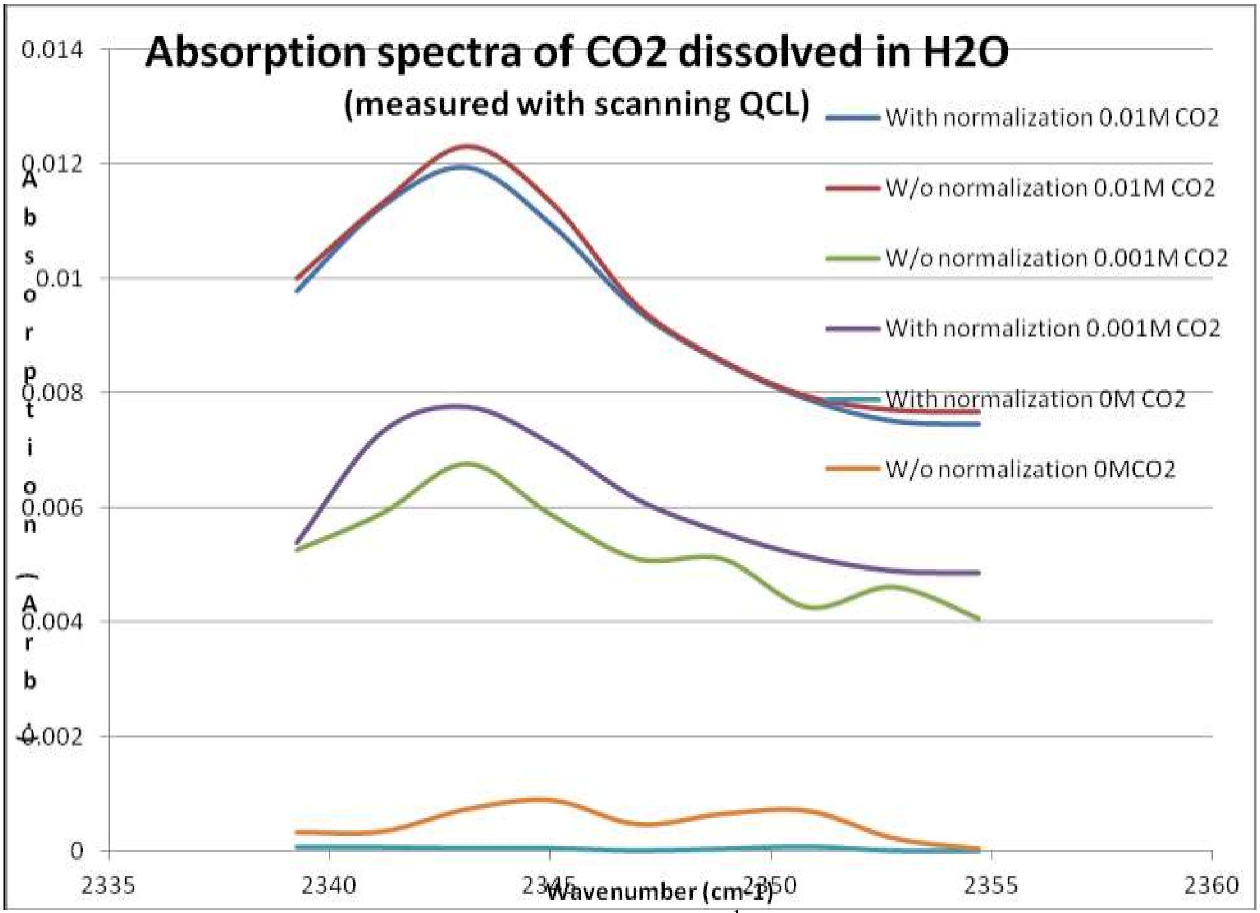


Figure 6. With single QCL laser scanning through 15cm^{-1} with one side at the peak, and the other side at the valley of the CO_2 absorption feature. Normalization here refers to real time normalization. The spectra w/o normalization is already corrected by ratio over the transmitted beam when there is no CO2 in water, and therefore no saw-tooth ramp function of the signal is shown.

Improved QCL modulation scheme results in lower cost and better signal to noise ratio

During phase I research, we have invented a new modulation scheme especially for QC lasers. Previously QC lasers' have only demonstrated limited tuning range well below 1% of the central frequency, usually only 0.2%. This means that to conduct absorption spectroscopy measurement of a broad feature, such as the CO_2 peak in water which has a linewidth of 10cm^{-1} (FWHM), we need two laser --- one parked at the peak and the other one parked at the valley of the absorption in order to measure the species. This translates into higher cost in terms of an extra laser, as well as combination optics (beam splitters and Hollow waveguide) that combine the two laser beams together. There is also loss of signal due to the combination optics and misalignment.

We carefully analyzed the thermal tuning behavior of QC lasers when operating under Continuous wave mode, and invented a new scheme that could tune over 1% of the central frequency in less than 100µsec[14]. The key inventions here are the modulation schemes as well as design of QCL waveguide and mounting schemes in order to achieve such wide tuning range.

The implications of this invention for our proposed QCL spectrometer for DIC and SC CO_2 measurement are:

- Instead of using two QCL lasers for measuring the CO_2 peak at 2,342cm^{-1}, i.e. first QCL parked at 2,342cm^{-1}, and second one parked at 2,352cm^{-1}, we could use only 1 QCL for this purpose. This cuts the cost, lower the requirement for dual wavelength combination optics and therefore saves the final system cost significantly. The simplified design also promises higher signal to noise ratio as we have demonstrated in our phase I research.
- The absorption lines due to gas phase CO2 could be used as a frequency marker for stabilizing the QCL frequency, eliminating the need for calibration samples or complicated wavelength meters in the final system.

We have had a proprietary filing with USPTO on this new invention (application number 61470048).

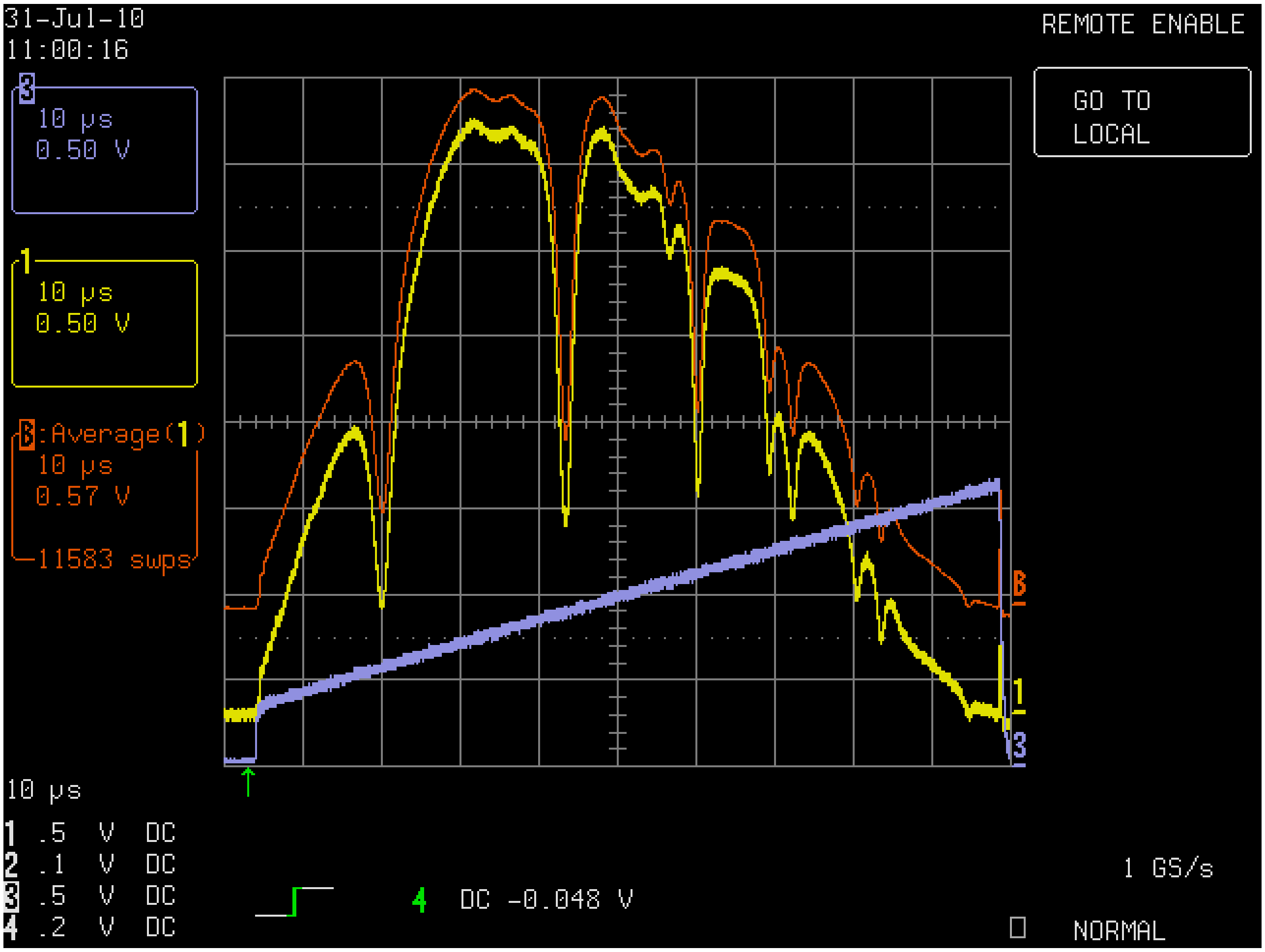


Figure 7. . Widely tunable DFB QCL enabled by advanced modulation technology were invented specially for the purpose of measurement broad spectroscopic features in condense phase. The tuning range is over 12cm^{-1}, the dipping peaks shown in the scan belong to the P branch of CO_2, and the spacing is about 2.1cm^{-1}.

Progress in QCL and MCT detector technology

Here, we wish to convince reviewers that QCL and Mid-IR technology is fast maturing and now able to get out of laboratory and into real world applications --- these are not results from our phase I effort but rather a big picture of the world-wide research in QCL and Mid-IR technology. In the past year, power of QCL lasers has reached *over 10W CW, and 100Ws in peak power with temperature of operation up to 200°C*. The wavelength coverage in the CO_2 band of 2,300~2,500cm^{-1} is available now for both pulsed and CW QCLs. At the same time, progress of uncooled or TEC cooled MCT detectors have also underscored Mid-IR spectroscopy applications for the real world. The majority results from our Phase I research and proposed phase II work are all based on uncooled or TEC cooled MCT detectors.

It is worthwhile to note that the cost of QC lasers and MCT detectors could go down significantly once quantity market need is created. The epi growth machine and processes for QC lasers are quite similar to other semiconductor lasers and LEDs, and therefore the driver right now is to find killer applications for QC lasers and MCT detectors.

Locating field test partners with potential regional CCS partnerships for phase II

We have shared the above results with potential regional carbon sequestration partnerships. Again, Dr. Katherine Romanak and Dr. Changbing Yang from the Bureau of Economic Geology (BEG), Texas of the SECARB regional partnership showed great interest in both the DIC and SC CO_2 measurement part. They could conduct parallel comparison measurement for DIC in with their commercial instrument and our machine in their laboratory. We have budgeted a $10,000 budget for this test in phase II at BEG. We also have search field testing opportunities for our instrument down in the bore-holes. For this purpose, we have contacted Paulsson Inc. (PI, Woodland Hills, CA). PI is currently conducting a DOE project using bore-hole deployed 3-D seismic imaging techniques to map CO2 reservoirs during CCS. We will test our instrument briefly with PI's bore-hole deployed seismic sensors at the end of the proposed phase II project.

To conclude, we have achieved positive results in phase I of the project. The proposed objectives have been met --- new invention enable lower cost and better reliability for the system to be built in phase II. We also addressed the concerns of the Review #3 and found extra capability of our instrument --- the new SC CO2 measurement function will open up immediate market in CO_2 *EOR based CCS applications.*

4. Phase II Project Technical Objectives, Approaches and Plans

Technical Tasks and Objectives outline

The phase II project will realize the following technical objectives or tasks for the first prototype QC laser spectrometer for DIC measurement. We will be leveraging our phase I R&D efforts and results (see section 3 above), the latest QC laser progresses, as well as molecular simulation results on DIC and SC CO_2.

Task 1. Design and build first QC laser spectrometer for underground DIC and SC CO_2 measurement.

Task 2. Build and acquire comparison test benches for the 1st QCL spectrometer above.

Task 3. Test the 1st QCL spectrometer above and formulate the design for the 2nd one.

Task 4. Build calibration database for the laser spectrometer under different sequestration scenarios, e.g. different salinity, pressure and temperature.

Task 5. With the 2nd prototype built above, conduct comparing field measurements with regional sequestration research team and 3-D seismic SC CO_2 imaging project using existing instruments.

Task 6. Conduct marketing efforts to locate first batch of trial customers

Strategic Design Approaches for the Spectrometer

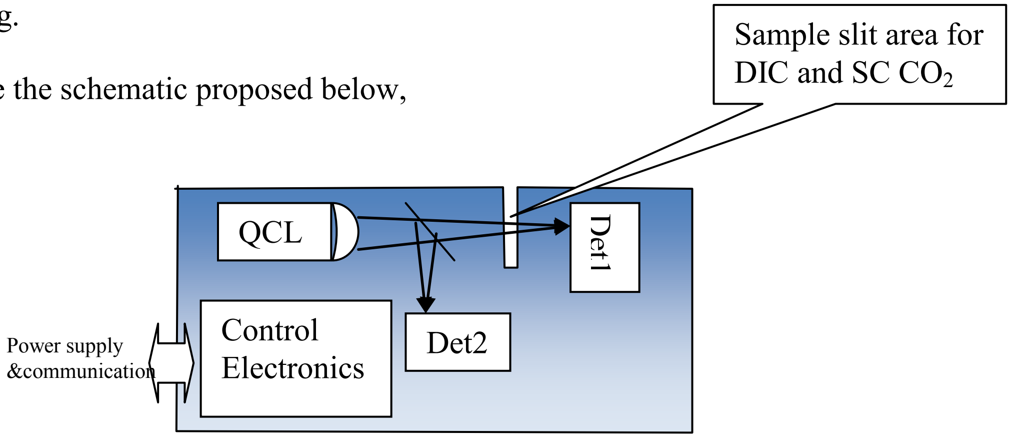
As pointed out by Review #3 on our Phase I proposal ---- besides the need to address the measurement of SC CO_2, the other major challenge of our proposed instrument is to be able to work under high pressure (1,200psi) and relatively high temperature (50~70°C).

We will design our prototype system around these requirements, i.e. high water pressure and temperature capability. More specifically, the laser and detector will be housed in an isolated housing that could stand a pressure of 1,200 psi and up to 80°C. The sample cell will be open to external fluid.

Our results in phase I already demonstrated the capability of the spectrometer able to work under room and slightly elevated temperature. The QC laser and detector will be TEC cooled to temperature just around 0°C, which should be achievable with dual stage TEC peltier cooler. Our laser will be working under very low duty cycle, therefore only 5W TEC could be used and the two detectors only need total of 4 Watt (2 Watt each) to maintain at temperature around 0°C.

We will first build one spectrometer and test it under laboratory simulated high water pressure and temperature conditions, then calibrate the system and design a 2nd spectrometer to real field testing.

We will use the schematic proposed below,



The shaded enclosure will have a outside dimension of 4"(W)x6"(L)x2"(H) and will be built with high pressure (>3,000 psi) steel material with high pressure sealed covers. The QC laser will be modulated over 20cm^{-1} to cover the peak and valley of the CO_2 absorption feature for measuring DIC and SC CO_2. The output of the QCL will be collimated, split and focused onto two detectors, i.e. Reference (Det2) and Absorption (Det1). The QCL, detectors' signal will be controlled and processed by the control electronics built inside the high pressure housing. It is designed that communication with outside is done with fiber optics to the well head, and power supply will be transmitted by cable from the well head down to the bore-hole. Other sensors such as pressure, temperature and pH could also be integrated into the system.

The DIC and SC CO_2 liquid samples will diffuse into the sample slit area where the QCL laser beam will pass through and probe the absorption. The sample slit area has a thickness of 300μm and will be separated from the main pressure housing using high pressure IR transmitting windows, e.g. Sapphire, for the QCL working at 4.3μm (~2,350cm^{-1}).

Phase II work plan

Year I

We will first address two technical objectives and tasks below in phase II of the project:

Task 1. Design and build first QC laser spectrometer for underground DIC and SC CO_2 measurement.

Subtask 1.1. Design the first QC laser spectrometer

Our first design will not include fiber communication and power delivery over long cables typically used in bore-hole seismic imaging. Instead, our first design will focus on delivering a system that could work under high pressure (up to 2,000 psi) and relatively high temperature (up to 100°C). This is to speed up the initial proof-of-principle process where the largest challenge we see is the ability to work under such harsh conditions. Fiber optical communication and power supply for deep bore hole use are expensive but with proven designs readily available for us to integrate once we prove that our design work under harsh conditions.

Subtask 1.1.1. Design and Build the widely modulated DFB QC laser source and dual detector system with normalization capability.

Subtask 1.1.2. Design the spectrometer system for DIC measurement under real sequestration conditions, i.e. high salinity, pressure and temperature.

Subtask 1.2. Build the first QC laser spectrometer.

We will build the first QC laser spectrometer around the designs we finished above. This system will have the features so that we could proceed not only perform tests, but also build calibration parameters around it so that DIC and SC CO_2 measurement will be accurate under different harsh conditions.

Subtask 1.2.1. Design and build the integrated DIC spectrometer system with self-contained single board computer interface.

Subtask 1.2.2. Take data and develop software to validate the effect of normalization and removal of matrix effect, i.e. minimal detection limit and accuracy.

Task 2. Build and acquire comparison test benches for the 1st QCL spectrometer above.

In order to conduct comparison test and build a calibration standard, we propose to build and acquire commercial test benches. A manometer type of DIC measurement machine will be acquired in our lab and conduct the cross-check comparison measurements. A SC CO_2 manifold will also be built to prepare SC CO_2 at various pressure and temperature, and make it available for our instrument to calibrate.

Subtask 2.1. Acquire a commercial DIC measurement machine, e.g. from LICOR, and add customized parts for automated calibration processes.

Subtask 2.2. Build the SC CO_2 manifold that provide SC CO_2 at various pressure and temperature, and available for our prototype to measure at the sample slit area.

Task 3. Test the 1st QCL spectrometer above and formulate the design for the 2nd one.

The test of the 1st QCL spectrometer will start at the end of year I and finish in the first Quarter of year II. We will also start to formulate the designs for the 2nd one.

Subtask 3.1 Test and calibrate the 1st prototype spectrometer

Test include pressure test (up to 2,000 psi), temperature cycle test (up to 100°C), and water tightness test. Fully calibrate the QC laser spectrometer for DIC under simulated brine sequestration conditions, e.g. different salinity, pressure and temperature

Subtask 3.2 Formulate the design for the 2nd prototype.

Task 4. Build calibration database for the laser spectrometer under different sequestration scenarios, e.g. different salinity, pressure and temperature.

Starting the 4th quarter of year I and into the 2nd Quarter of Year II, we will build the database of DIC and SC CO_2 measurements as we test the first prototype against the comparison test benches built in Task 2.

Subtask 4.1 Build calibration database for the 1st prototype.

Year II

Task 3. Test the 1st QCL spectrometer above and formulate the design for the 2nd prototype

The test of the 1st QCL spectrometer will start at the end of year I and finish in the first Quarter of year II. We will also finish design and building the 2nd prototype in the end of the 2nd Quarter of year II. This includes the calibration test for the 2nd prototype against our comparison test benches.

Subtask 3.3. Design the 2nd prototype
Subtask 3.4. Build the 2nd prototype
Subtask 3.5. Test the 2nd prototype
Perform the same tests as done to 1st one in Subtask 3.1.

Task 4. Build calibration database for the laser spectrometer under different sequestration scenarios, e.g. different salinity, pressure and temperature.

Subtask 4.2 Build calibration database for the 2nd prototype.

Task 5. With the 2nd prototype built above, conduct comparing field measurements with regional sequestration research team and 3-D seismic SC CO_2 imaging project using existing instruments.

In the 3rd quarter of year II, we will send out the 2nd prototype to other laboratories for field test. For the DIC field measurement, we will send it to BEG of Texas for test. For the bore-hole test, we will arrange field test with our collaborator, Paulsson Inc., in their CO_2 underground bore-hole seismic imaging field.

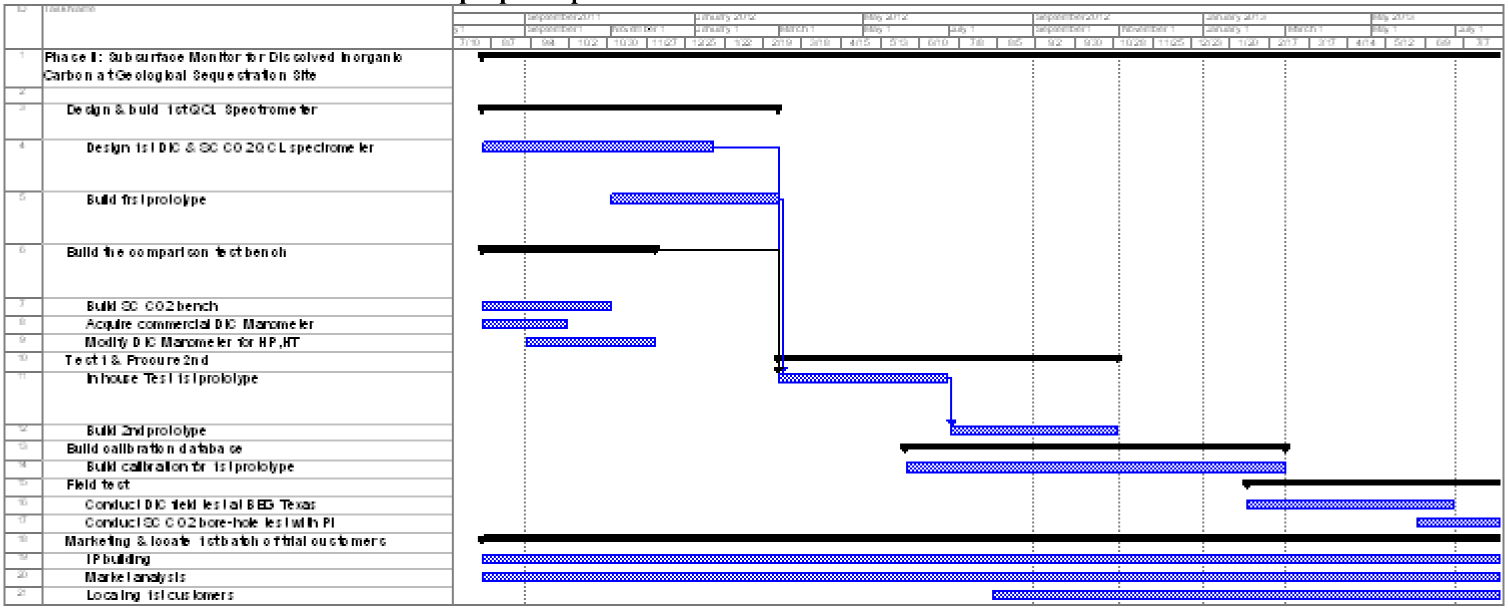
Task 6. Conduct marketing efforts to locate first batch of trial customers

We will then address the product marketing issue by conducting comparison demo trials and locate first batch of trial customers in phase II of the project.

Phase II Milestones and Schedules

Gannet chart of the proposed project is shown below.

Table 3. Gannet Chart of the proposed phase II



Phase II of the proposed project will have to four major milestones that we plan to achieve at the end of tasks 1 and 2.

Milestone 1. By the end of the 3rd quarter, complete the 1st prototype and testing the ability to work under hard conditions outline above.

Milestone 2. By the end of 4th quarter, demonstrate that the ultimate sensitivity and ability to measure DIC and SC CO_2.

Milestone 3. By end of the 6th quarter, deliver the 2nd prototype that could conduct automatic unattended measurements.

Milestone 4. By the end of the 2nd year, complete field test for 2nd prototype and able to locate first trial customers at CO_2-EOR CCS sites.

The total budget will be $981, 267 for the proposed tasks above in the phase II project. SGTC will cost share 20% of the budget and with the rest coming from DOE.

Major equipment to be acquired or constructed for the Phase II project

3 QC lasers systems with wide and fast modulation functions, and 2 of these will be integrated into two DIC spectrometer systems, value $85K total.

3 dual Detector systems with normalization functions, and 2 of these will be integrated into two DIC spectrometer systems, value $45K total.

2 DIC spectrometers that will work under high pressure, salinity and temperature conditions.

5. Related R&D efforts and results

Coupling QC lasers into hollow waveguide (HW)

We demonstrated and first reported in literature that the coupling efficiency is over 50% for semiconductor epi lasers, e.g. QC lasers, into HW due to QC laser's high brightness[15]. The transmission loss of HW is also quite low, only about 1-2dB/meter, making it an ideal waveguide to carry and deliver two different wavelength QC lasers over a short distance, e.g. ~10cm, while conserving the power. SGTC, as subcontractor for the DOE-RPSEA project titled 'Novel Gas Isotope Interpretation Tools to Optimize Gas Shale Production' (DE-AC26- 07NT42677), develops the online CO_2 isotope ratio sensor for GC using QC laser and Hollow Waveguide.

Pulsed QC laser detection of gas molecules.

We have built pulsed drivers for QC laser pulsed operation. We also have built sample and hold circuitry for detecting pulsed QC laser signals with reduced noise. The results are presented in our effort/publication to measure CO2 gas molecules in the hollow waveguide with a pulsed QC laser[15]. An in-house dual channel Peak Sample and Hold circuitry (using TI's OPA615 special Transconductance amplifier) have also been fabricated already for our other on-going project of detecting gas phase CO2 isotopomers in hollow waveguide as shown in figure 5. We will fabricate two more such boards for our dual wavelength measurements with pulsed QC lasers.

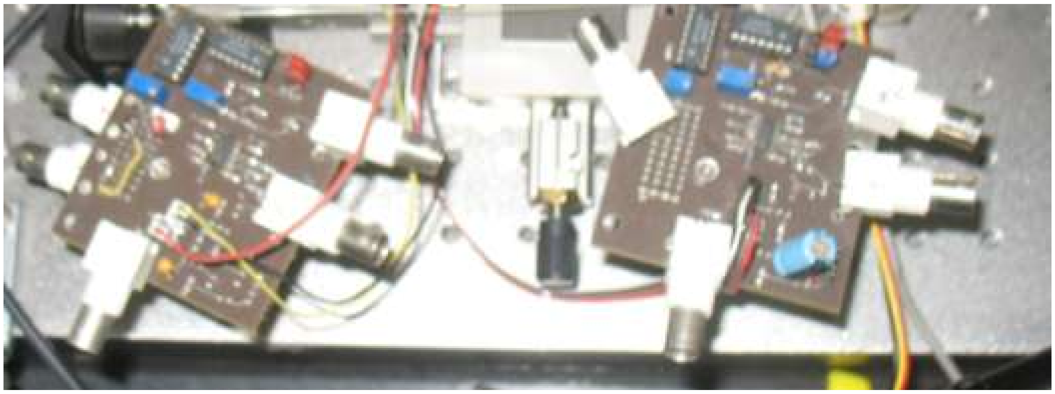


Figure 8. Peak Sample and Hold PCB pair for dual channel pulsed QCL DAQ.

In house designed QC Laser driver and TEC controller

The QC lasers need a driver that has much higher compliance voltage than regular Near-IR semiconductor lasers. We have designed out in-house pulsed QC laser driver for this purpose. The wavelength of a QC laser needs to be stabilized in the vicinity of a chosen CO2 absorption feature. We also integrated a TEC controller with our QC laser driver. A LD + TEC driver based on Wavelength Electronics WLD3343 laser diode driver chip and the HTC3000 TEC controller were built. The WLD3343 has a bandwidth of 2M Hz, sufficient for 100s Hz modulation. The HTC3000 TEC controller could control a total of 18W of heat/cooling power to the Peltier element for the TEC control of the QC laser.

Molecular simulation of DIC components for Underground Brine CO_2 Sequestrations

We collaborated with the Material Simulation Center (MSC) of Caltech, and in October, 2009 MSC got a 3-year award from DOE's "Geologic Sequestration Training And Research" program DE-FOA-0000032 for the simulation of the changes of the Mid-IR spectra of DIC species in brine water under extreme conditions. Their results will guide the development of the prototype instrument in our phase II project by predicting the change of spectra under extreme conditions, i.e. high pressure and relatively high temperatures. With FTIR only, it is quite hard to obtain the spectra under such conditions. The research at Caltech has also started the simulation of SC CO_2 Mid-IR spectra under various pressure and temperature conditions, and this simulation will also help our instrument's capability to measure underground injected SC CO_2.

Atmospheric sensing for CO_2 MVA

Sheeta Global together with a team from California Institute of Technology worked on development of a low-cost long-range atmospheric CO_2 monitor. This work was funded by DOE through an STTR grant (see section 9). The long-range CO_2 monitor developed in that project performs detection of CO2 in the near-IR, using the frequency modulation technique.

Although the proposed CO2 monitor will perform detection in the mid-IR it can still use several electronic circuits developed for the long-range near-IR monitor. These include the laser driver (modified for pulsed QCL) and temperature control circuit.

6. Principal Investigator and other Key Personnel

This project involved two scientists: PI Dr. Sheng Wu, and co-PI Dr. Andrei Deev, along with part time support from our engineering staff.

Dr. Sheng Wu received BS in Chemistry and BS in Physics from Peking University in 1992, MS in Environmental Engineering and Science from Caltech in 1995, and Ph.D in Chemistry from Caltech in 1999. In 1999-2009, Dr. Wu had been working at Caltech as a Postdoc, Scientist and Senior Scientist. He has also been a product manager at CASIX/JDS Uniphase, and Photop Technologies. Currently, Dr. Wu works as a Senior Research Scientist at Power, Environmental and Energy Research Institute and as Research Scientist at Sheeta Global Technologies. Dr. Wu's expertise includes laser design and development, opto-mechanical design, and development of analytical instrument. He developed the Timeplate Tripler nonlinear optical converter which won the Laser Focus World Commercial Technology Achievement (CTA) Finalist Award in 1999. His current research mostly focuses on development of trace gas sensors for environmental monitoring and gas chromatography, and optical isotope analyzers.

Dr. Andrei Deev received MS in Physics from Moscow Institute of Physics and Technology in 1997, and Ph.D. in Physical Chemistry from Caltech in 2005. In 2005-2009 Dr. Deev held a postdoctoral fellowship at Chemistry Department at Caltech. Currently Dr. Deev works a Senior Research Scientist at Power, Environmental and Energy Research Institute and as Research Scientist at Sheeta Global Technologies. Dr. Deev's expertise includes laser spectroscopy, mass spectroscopy and gas chromatography. His current research mostly focuses on development of trace gas sensors for environmental monitoring and gas chromatography, and optical isotope analyzers.

7. Facilities and equipment

The proposed research activities will be carried out at the SGTC facility. The facility consists principally of office and laboratory space. SGTC has a 2,100 square feet lab facility located in Covina, California. The facility includes an optical lab with equipment necessary for prototyping of optical instruments, and chemistry lab and ventilation hoods for wet chemistry experiments. This includes DFB and tunable diode lasers, a pulsed thermoelectrically-cooled QC laser with a set of control electronics and many MCT detectors, near-IR and mid-IR detectors, oscilloscopes, data acquisition boards, soldering stations, and software for mechanical and electronics circuit design. Manufacturing of printed circuit boards (PCB) will be done by an outside company at the cost less than $1000.

Besides the regular facilities and equipment, we want to emphasize here that we already have the unique capital equipment (>$5k/each) and experiences needed for the proposed research. These equipment and experiences provide a good starting platform for our proposed research.

8. Commercialization Plan

See separate file attached.

9. Company and commercialization history, past/existing government grants

Established in 1998, the SHEETA Global Technology Corporation (SGTC) has quickly emerged as an active small-scale R&D company dedicated to global energy and environment research. SGTC has a track record of performing unique technical laboratory studies with a focus on those having an application of new chemical products and concepts. SGTC also has developed new technologies that have led to several patents.

The vision of SGTC is to integrate the latest developments in Chemistry, Chemical Engineering, Material Science, Geochemistry to accelerate commercialization and technology transfer in the energy section. During the past 10 years, SGTC has two spin-off commercialization entity, namely GeoIsoChem (www.geoisochem.com) and ChemEOR (www.chemeor.com). Geoisochem is an industrial leader in isotope modeling and analysis, providing quality isotope analysis for clients. Currently, Geoisochem is working with California Institute of Technology to perform a DOE-RPSEA project titled ‘Novel Gas Isotope Interpretation Tools to Optimize Gas Shale Production’ (DE-AC26- 07NT42677). ChemEOR has become a leading service company in performance oilfield products. Currently, SGTC is also working on development of technologies for carbon dioxide monitoring and hydrogen storage.

SGTC has received the following SBIR grants from government in the past two years,

1. DOE STTR, grant # "DE-FG02-08ER86361", Title "Low Cost Open-Path Instrument for Monitoring Surface Carbon Dioxide at Sequestration Sites"
2. NSF SBIR, grant # "IIP-0912856", Title "Diamondoid-Containing Carbon Nanostructures as Hydrogen Storage Materials"

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