A STUDY OF CARBON DIOXIDE DIFFUSIVITY

THROUGH SAND

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A STUDY OF CARBON DIOXIDE DIFFUSIVITY

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Abstract:
The purpose of this study was to measure the diffusion of carbon dioxide through sand and determine the viability of using cheap carbon dioxide sensors to measure diffusion. The data for the study was collected with the use of the K-30 and K-33 ELG carbon dioxide sensors in a diffusion cell set up made from PVC pipe fittings. The carbon dioxide concentration data was taken using software known as "Gaslab" and was interpreted using a program written by the author. The program was designed to run simulations of the column with given diffusivities, and use an optimizer to find the diffusivity that resulted in the least deviation between simulation and data; this diffusivity would then be taken as the diffusivity of the material in the column. Three series of experiments were run, the first quantified the rate of leaking within the column, the second validated the use of the column to measure diffusivity by measuring the diffusivity of carbon dioxide in air, and the third measured the diffusivity of carbon dioxide through dry sand sieved to ASTM 40-80 grain. The measured diffusivity of carbon dioxide through air matched the literature diffusivity and the diffusivity of carbon dioxide through the sand used was found to be $(3.5 \pm 0.49) \times 10^{-7}$ m^2/s. These results suggest that the column set up was adequate for measuring the diffusivity of carbon dioxide through the sand sample, and could be used to measure the diffusivity of carbon dioxide or other gases through sands or porous materials.

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CHAPTER I

INTRODUCTION

Background

Carbon dioxide injection for the enhanced recovery of oil has been a topic of interest lately for

two major reasons. The first of these reasons is economical; it can result in the production of

much more of the remaining oil in the reservoirs than primary and secondary recovery methods.

The second reason is environmental; carbon dioxide is one of the more potent and prevalent

greenhouse gasses and injecting it into oil reservoirs can prevent it from contributing to the

radiative forcing of the atmosphere [13].

Objective

While carbon dioxide injected into a reservoir is likely to stay there if the geological seal that kept

the hydrocarbons in place is intact, if the seal has been damaged by oil or gas production

operations, it is possible that it could leak back up through the ground into the atmosphere. The

purpose of this study is to measure the diffusivity of carbon dioxide through dry sand, which can

be used to quantify the rates of leaking in locations with similar soil characteristics.

Literature Review

The experimental work performed by the author focuses on evaluating the diffusion coefficient of carbon dioxide through air-saturated sand. There are a variety of studies that have been done measuring diffusion through various types of porous media, and the experimental methods and set up used in these studies were used as inspiration for the experiments performed by the author. Most of the experimental set ups in the papers consulted involved a column of porous or packed material situated between two reservoirs of gas, with concentration measurements being taken over a period of time from the gas reservoirs via gas chromatograph. In the paper "Diffusion and Production of Carbon Dioxide in Bulk Corn at Various Temperatures and Moisture Contents", the diffusivity measurements were taken using a horizontally oriented column packed with corn situated between two gas chambers that were kept at equal pressures. Due to the organic nature of the column packing, a source term was added to Fick's Second Law to describe the problem. They also solved this differential equation numerically with the finite difference method, utilizing a simple algorithm to find the effective diffusivity coefficient [3]. E. Jacops et al utilized reservoirs filled with a mixture of gas and water, though still at equal pressures so they could be sure the clay sample they used stayed water saturated throughout the experiment while still being sure there was no advective flux. This set up was also one of the only ones vertically oriented [4].

Some of these set ups, however, involved only a single gas reservoir connected to the column of porous or packed material with concentration measurements being taken at multiple points inside of the column rather than from the reservoir. In a paper by G. Shunmugam et al., the experimental set up described features a diffusion cell made up by a gas bulb and a grain column with a sampling port located in the grain column [1]. D. Pokhrel et al utilized a vertical system with the diffusing gas beneath a media compartment that had three spaced gas sampling ports and was supported by a wire mesh sitting on a perforated plate [5]. T. Bardakci and F.G. King utilized the steady state diffusion measurement method across a long, very thin stainless steel column packed with glass beads that had been sintered in a furnace at 793 K [2]. R. Islas-Juárez et al also used a

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set up with only one gas reservoir, and had four spaced sampling ports in the column to regularly take measurements from. This set up was also a somewhat unique case in that the porous media involved was completely saturated in hexane prior to the experiment and the column is set up vertically [8].

Still other set ups in the studies referenced for inspiration used different set ups and experimental methods. In their experiments, T. Nakano et al used chambers on the ground with carbon dioxide or methane to measure gas fluxes via soil-atmosphere diffusion [10]. While T.E. Larson and D.O. Breecker used a familiar packed column set up, their set up had no gas reservoirs and was a flow-through system that was set up to measure adsorption effects and worked from a model that included convection and diffusion terms [11]. Among these set ups, the ones used by M.E. Aguilera et al in their study of diffusion through wedges had the most unique configurations. Their set ups all involved diffusion through square shaped capillaries, and had a geometry with a liquid pool below a section of carbon dioxide, one with a shrinking liquid bridge between bubbles of carbon dioxide, and finally another with a shrinking bubble of carbon dioxide within a section of liquid. Diffusivity data could then be calculated from the size of the pool, liquid bridge, or shrinking bubble [6].

CHAPTER II

THEORY

Direct Injection of Carbon Dioxide

After the primary and secondary recovery at an oilfield, more than half of the original oil in the

well can remain. One of the more advantageous methods for tertiary recovery after this is the use

of carbon dioxide injected into the well at high pressure. This has two primary benefits, the first

being additional hydrocarbon recovery and the second being the sequestration of carbon dioxide.

Carbon dioxide has a few properties that make it particularly suited to use in enhancing oil

recovery. It "improves oil recovery by lowering interfacial tension, swelling the oil, reducing oil

viscosity, and by mobilizing the lighter components of the oil. [15]" Injection can also be utilized

in gas fields as well. Because it is denser and more viscous than natural gas at reservoir

conditions, when injected at the bottom of the formation it will migrate downward and avoid

mixing with the natural gas in the formation [14]. While it can be used to greatly increase the

recovery of oil from wells, the cost of the carbon dioxide to use as an injection gas can be a

limiting economic factor. As a method for sequestration though, injection in oil reservoirs is

appealing because, so long as the natural seal that has trapped the hydrocarbons in the first place

isn't damaged in the production process, the reservoirs can be used to hold the injected carbon

Dioxide indefinitely [13].

Fick's First and Second Laws

Fick's First Law is used to describe the flux of a material in a system. Its one dimensional representation follows;

$$(J_A/A)_x = -D * (\partial C_A/\partial x)$$

Where:

- $(J_A/A)_x$ is the molar flux at steady state and constant temperature and pressure

- D is the diffusion constant, or diffusivity

- $\partial C_A/\partial x$ is the concentration gradient of the species A

The program written by the author to interpret the data solves the differential equation numerically. Flux calculations are done for the chambers to maintain the inventory of carbon dioxide present, since those differential elements are not the same size as those in the column body. A forward difference approximation was used for the calculation of the flux in and out of the chambers.

$$(J_A/A)_x = -D * \frac{C_{A,i} - C_{A,i+1}}{dx * 0.5}$$

The multiplier of 0.5 comes out of the assumption that the chambers of the column are well mixed. Since the concentration is assumed the same all the way through the chamber up to the boundary, the space that the gradient is measured across is only half of a differential element, the space from the top of the chamber to the middle of the first column element.

Fick's Second Law can come out of the mass continuity equation by eliminating the generation

term and only considering molecular transport. The mass continuity equation for one dimension is

as follows;

$$\frac{\partial C_A}{\partial t} + \frac{\partial (C_A U_x^*)}{\partial x} = \dot{\psi}_G + D\frac{\partial^2 C_A}{\partial x^2}$$

Where:

- $\partial C_A/\partial t$ is the accumulation term for species A

- $\partial(C_A U_x^*)/\partial x$ is the input/output convection term based on the molar velocity of the species in the

x direction

- ψ_G is the generation/depletion term for species A

- D is the diffusion constant, or diffusivity

- $\partial^2 C_A/\partial x^2$ is the second derivative of the concentration of species A in the x direction

In the column, it is assumed that there is no bulk transport of any species within the column body

and that there are no reactions taking place to replenish or deplete carbon dioxide within the

column. With these assumptions, the continuity equation simplifies to Fick's Second Law of

Diffusion as follows;

$$\frac{\partial C_A}{\partial t} = D\frac{\partial^2 C_A}{dx^2}$$

When evaluating this equation numerically, the program uses a forward difference approximation

on the time derivative, and a central difference approximation on the second spacial derivative

with the resulting equation found in the program.

$$\frac{C_{A,i+1} - C_{A,i}}{dt} = D\frac{C_{A,j+1} - 2C_{A,j} + C_{A,j-1}}{(dx)^2}$$

Where the subscript "i" denotes the location of an element in the time direction and "j" denotes

the location of an element in the x direction. Where omitted, subscripts are assumed to be for the

current step.

Model of Column Set Up

The model of the column consists of three major sections, the bottom chamber, the column body, and the top chamber where the chambers are the tee sections in the picture above. The contents of the bottom and top chambers are always assumed to be well mixed and it is assumed that Fickian Diffusion is the only transport phenomena taking place in the column body. In the column runs with sand, there is a screen in place between the body and the valve to prevent sand from falling

into the valve or bottom chamber. It is assumed that this has a negligible effect on the calculated diffusivity.

Heuristic Direct Search Optimizer

The author chose to interpret the diffusivity data by running a model of the column at varying diffusivities until the deviation between the data and the model data was minimized. This process could be automated with the use of an optimizer, and the author chose to use a heuristic direct search optimizer for this task. A heuristic direct search optimizer will only use function values, no derivatives are necessary, to find the maxima of a function. Traditionally, the optimizer uses an initialization value (x_{base}) on the decision variable as well as an initial amount to change the decision variable by (Δx) from iteration to iteration. After incrementing x_{base} by Δx to make x_{new}, the optimizer then checks the function value at x_{new} against the value at x_{base}. If the value at x_{new} is lower than the value at x_{base}, x_{new} will become the new x_{base} and Δx will be multiplied by an expansion factor. If the value at x_{new} is higher than the value at x_{base}, the Δx value is multiplied by a negative contraction factor and x_{base} remains unchanged. The convergence criterion for the process is on Δx, once it falls below a threshold value the optimizer is considered to be converged.

Due to the nature of the problem however, the search works somewhat differently. Because the range on diffusivity is so wide, the range of expected diffusivities for the sand test case spanned three orders of magnitude, the version of the heuristic direct search optimizer used by the program works around multiplication rather than addition. When checking for the next value of x_{new}, x_{base} is instead multiplied by a factor that will be denoted as xV. If the objective function is lower at x_{new} than at x_{base}, then x_{new} becomes the new x_{base} and xV is raised to the power of the expansion factor. If the objective function is higher at x_{new} than at x_{base}, then x_{base} does not change and xV is raised to the power of the contraction factor. This modified procedure allows the optimizer to search quickly through multiple orders of magnitude.

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The following is a graph of the sum of squared deviations vs the diffusivity that was used to get a general idea of how the two are related over a range of potential diffusivities that could be encountered in the column. As this study was conducted before the column set up was in place, the sets of data used to make the sum of squared deviations (SSD) were both generated by the concentration data analysis program, with the diffusivity of the "data" being set at 10^{-6} m^2/s and the optimizer varying the "simulated" set. This optimizer was simpler than the heuristic direct search, it started with a diffusivity of 10^{-9} m^2/s and multiplied the diffusivity by the fourth root of 10 until the sum of squared deviations significantly changed, and then it multiplied the diffusivity by a smaller factor to see how the sum of squared deviations relates to the diffusivity close to the optimum.
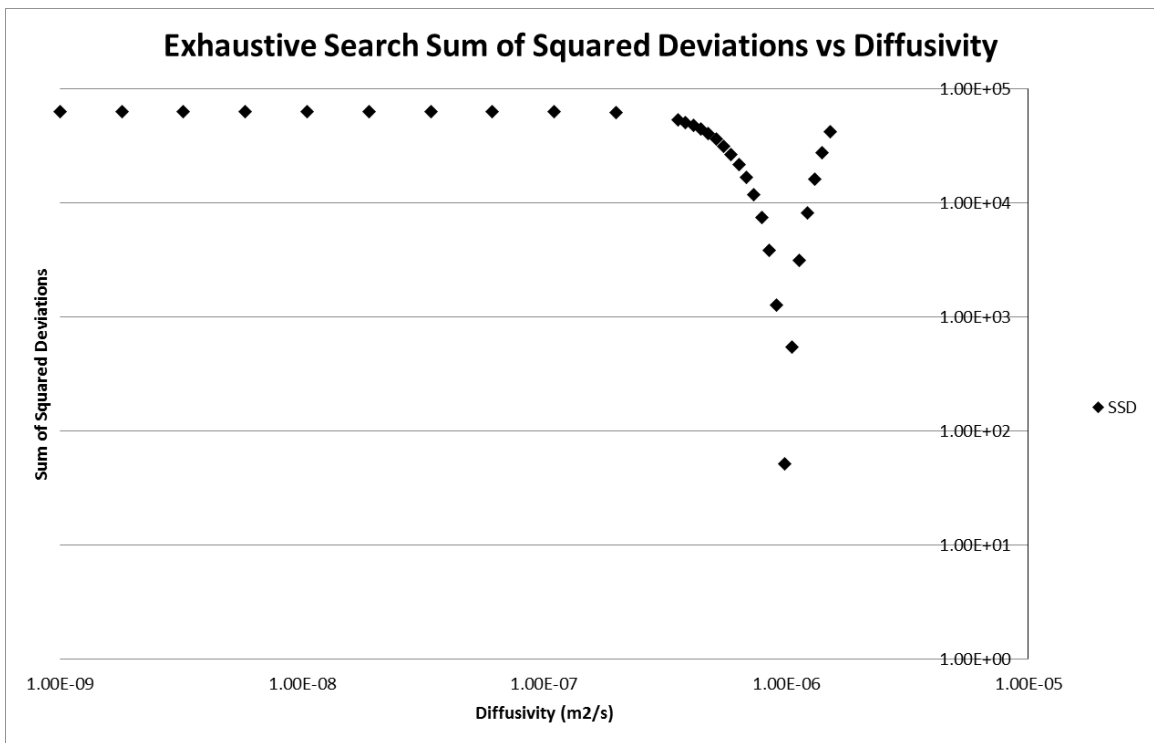

Figure 2: Logarithmic Plot of the SSD Plotted Against Diffusivity

As the diffusivity increases from 10^{-9} m^2/s, the SSD actually remains essentially constant up to about 3×10^{-7} m^2/s because the concentrations at the top and bottom of the column aren't changing

significantly with diffusivity in the time span of the simulation. As the trial solution diffusivity approaches 10^{-6} m²/s, the SSD rapidly approaches zero. Once the trial solution diffusivity is above 10^{-6} m²/s, the SSD increases again without bound and at a high rate.

Each time the heuristic direct search optimizer is initialized, it evaluates the SSD at a variety of points to get a starting place for the direct search. When using the optimizer for experiments with sand, these points were from diffusivity = 10^{-8} m²/s to 10^{-5} m²/s. After running the initial diffusivities, the optimizer finds the one with the lowest SSD and uses that as the base point for the actual heuristic direct search.

Concentration Data Analysis Program

The program for analyzing the concentration data applies principles from the heuristic direct search optimizer and Fick's laws of diffusion to the model to simulate the diffusion going on within the column and find the diffusivity that makes the simulation best match the data from the sensors. There are two different versions of the program, one that is used to determine the leak rates from the top and bottom chambers, and one that is used to measure the diffusivity of whatever fills the column body.

In order to validate the choice of parameters used in the column simulation, a separate program was written that would simulate the heat transfer in a piece of metal. Because the boundary's conditions in this separate simulation are simpler, it is possible to analytically solve its differential equation so the numerical simulation could be compared to the analytical one. At the conclusion of the simulation, the percent difference between the temperatures at each location in the metal between the two simulations was calculated.

The diffusivity version of the program starts by initializing xV, the expansion factor, and the contraction factor. After setting these parameters for the direct search, the program then begins the serach by simulating the column with a predetermined set of diffusivities (a different set was

used depending on whether there was air or sand in the column), to find a diffusivity to begin the search at. A flowchart of this simulation procedure can be found in the following figure.

Figure 3: A Flowchart of the Simulation Procedure

After each of these runs, the simulated concentrations in the chambers are compared to the data from the sensors. To establish the deviation between the sets, at each time point the program takes the difference between the simulated concentration and the recorded concentration, squares it, and adds it to a running total to make a sum of squared deviations for the run. The diffusivity that had the lowest sum of squared deviations is then used as the base diffusivity in the optimization. At this point, the heuristic direct search optimizer begins its serach, using the diffusivity as the decision variable and the sum of squared deviations between the data and the simulation as the objective function to be minimized.

Because the column apparatus leaks, a version of the program that would quantify this leaking was necessary for the interpretation of the data from any runs that took longer than a few hours. For the purpose of this version of the program there are two sections, the bottom chamber and everything else. Combining the top chamber and column body was necessary for the program for two reasons; the first reason being the apparatus had nothing separating the top chamber and column body so the leaking from each section could not be isolated and the second being that there was no way to put a sensor in the body section of the apparatus even if it could be isolated. There were two major reasons leading to the author's choice to include the column leaks as diffusivity terms within the simulation. The first reason was it was impossible to know the size and location of the leaks, so a more representative model was not possible, as its parameters could not be known. The second reason was when the leaking was modeled as diffusion into a separate column, the resulting diffusivity from the leak test measurements could be directly compared to the diffusivities obtained from the control and sand experiments.

The leak version of the program works similar to the way the diffusivity version works but the premise is somewhat different. While the diffusivity version takes the top and bottom section data from a run and tries to match it with a simulation, the leak test version takes data from just one section at a time. It then works by going through a simulation of the column and tries to minimize the deviations between the bottom section in the simulation and the data. This operation mode means that the diffusivity result is the diffusivity that would be required of the column material to result in the same loss of material as the leak.

CHAPTER III

EXPERIMENTAL SET UP AND METHODS

The diffusion experiments were carried out in a cell made from PVC pipe sections, two PVC tees (which will be described as chambers), a ball valve, and a length of two-inch diameter pipe. The PVC pipe section was used as the column body filled with sand, or in the case of the control experiments air. A small filter made from two rings holding together a circle of 200 mesh screen supported the column of sand within the column body. A ball valve separated the column body from the bottom chamber and was used to isolate the bottom chamber while it was being filled with the test gas, a 2000 ppm carbon dioxide mix in nitrogen. The top chamber was connected directly to the column body.

Not pictured above, is the gas cylinder and tubing used to deliver the gas to the bottom chamber. The end caps on the bottom section were held in place by a combination of caulk and the all thread pieces with the hand screws. The all thread pieces in the bottom also provided a way to fill the bottom chamber with the test gas without pressurizing it; prior to filling the bottom chamber one of the all thread pieces could be removed so displaced air had a place to escape to. The bucket on the right contains the dried and sieved sand that was in the primary diffusion experiments. The white circle on the stand holds the mesh section that was used to keep the sand from falling through into the valve and bottom chamber, and was squeezed between the column body and the ball valve. The white object with the tube on the bottom right of the photo is an air pump that was used to flush the test gas from the column following every run. The thin tubing

coming up from the top chamber was used to relieve pressure during the flushing process, and was capped during the experiments.

Figure 5: A Close Up Picture of the Bottom Chamber

Pictured above is the bottom chamber after it was removed from the rest of the column. A K-33 ELG carbon dioxide sensor and the wiring to a small fan can be seen inside. The top section looked the same, though it had the holes in the end caps drilled for all thread taped over, a pressure relief tube, and a K-30 1% carbon dioxide sensor inside. The K-30 and K-33 ELG sensors were chosen in part so the author could determine whether or not relatively cheap sensors could be used to gather good diffusivity concentration data. The concentration data in the experiments were taken using a program called Gaslab.

Validation Program

Prior to setting up the experiments, the author wrote a program to validate the model parameters chosen in the simulation of the column. This program worked by simulating the heat transfer in a

bar of material with a numerical solution of the model equation and an analytical solution and comparing them. The following model parameters were used in the validation simulation.

Table 1: Validation Program Default Parameters

Parameter	Value	Units
Thermal Diffusivity	10^{-6}	m^2/s
Bar Length	1	M
Boundary 1 Temperature	0	°C
Boundary 2 Temperature	0	°C
Temperature (time=0, x)	$60*\sin(\pi x)$	°C
Simulation Time Step	1	second
Simulation Space Step	.01	meter
Total Simulation Time	10000	seconds

The thermal diffusivity constant and bar length were chosen to roughly approximate what was expected from the physical system to be put in place. The simulation time step and space step sizes were later used as guidelines when analyzing the data in later experiments and the total experiment times were generally within about an order of magnitude of the validation total simulation time. After executing the control and sand experiments, the validation program was rerun two more times, each time to more closely mimic the parameters used for the experiments. To mimic the sand conditions, the follower parameters were used in the validation simulation.

Table 2: Validation Program Sand Mimic Parameters

Parameter	Value	Units
Thermal Diffusivity	$4x10^{-7}$	m^2/s
Bar Length	1	M
Boundary 1 Temperature	0	°C
Boundary 2 Temperature	0	°C
Temperature (time=0, x)	$60*\sin(\pi x)$	°C
Simulation Time Step	30	second
Simulation Space Step	.01	meter
Total Simulation Time	86400	seconds

For this run, the thermal diffusivity was set at a value closer to what the sand experiments were yielding, and the bar length was reduced. The number of space steps in the simulation was also

reduced, and the time step length was increased to mirror the resolution given by the sensors. In order to mimic the conditions in the control tests with the column containing only air, the following parameters were used.

Table 3: Validation Program Control Mimic Parameters

Parameter	Value	Units
Thermal Diffusivity	1.4×10^{-5}	m^2/s
Bar Length	1	M
Boundary 1 Temperature	0	°C
Boundary 2 Temperature	0	°C
Temperature (time=0, x)	$60*\sin(\pi x)$	°C
Simulation Time Step	1	second
Simulation Space Step	.0289	meter
Total Simulation Time	1800	seconds

This run had its thermal diffusivity increased to a value representative of the control test results, a reduced number of space steps, and a reduced bar length. The simulation time step was kept at just one second because a value representative of the sensor resolution would result in a diverging solution.

At the conclusion of each of these experiments, the percent difference between the temperatures at each space step between the analytical and numerical simulations was used to determine the appropriateness of the model parameters.

Leak Test Experiments

When trying to get the column set up sealed it became apparent early on that the leaking of gas in and out of the column could be mitigated, though not eliminated. Since the test gas is inert, this did not pose a safety concern but it did need to be quantified and accounted for. Since the valve is the only way to isolate sections of the column, the leaking from the column body and top chamber had to be combined. The author used the following experimental procedure to quantify the rate of leaking.

1. Open the main column valve and make sure the pressure relief tubing at the top of the column

is unobstructed.

2. Open the valve to the test gas cylinder and set the regulator exit pressure at 50 psig.

3. Watch the readings from the bottom and top carbon dioxide sensors. Once readings have been stable for 15 minutes, close the valve on the test gas cylinder and cap the pressure relief tubing at the top of the column.

4. Record carbon dioxide readings from Gaslab at 30 second intervals over the next 72 hours.

5. Remove the test gas tubing from the bottom chamber and the cap on the pressure relief tubing at the top of the column. Use an air pump to flush the test gas out of the column until the carbon dioxide sensor readings have returned to a baseline value.

From there, the data was then processed via the author's concentration data analysis program. The program interprets the concentration data as if the leak from each section was diffusion through a column with the same dimensions as the main column body. This interpretation resulted in pseudo diffusivity constants that could then be compared to the constants coming from the interpretation of the control and sand test data, so the significance of the leaking could be understood.

Control Test Experiments

Once the leaking from the top and bottom of the column had been quantified, the set up and model could then be tested via two sets of control experiments. Each used the same procedure, but one set was run with the column body containing only the sand screen and the other set was run with the column body completely empty. The control experiments without the sand screen could then be used to verify that the set up and model were valid while the control with the sand screen would show the magnitude of the screen's interference with the test gas diffusion into the column body. The author used the following experimental procedure for the control tests.

1. Close the main column valve and make sure the pressure relief tubing at the top of the column is capped.

2. Remove one of the all thread pieces from the bottom chamber to relieve pressure.

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3. Open the valve to the test gas cylinder and set the regulator exit pressure at 50 psig.

4. Let the test gas flow into and through the bottom chamber for 15 minutes. At the conclusion of this time, close the gas cylinder valve and put the all thread piece back into the chamber.

5. Let the column sit for 15 minutes to allow full mixing in the bottom chamber.

6. Set Gaslab to start recording in 30 second intervals for the next 24 hours and open the valve to the column body.

7. At the conclusion of the control test, remove the pressure relief cap and use the air pump to flush out the test gas from the column.

At the end of the experiment, the concentration data would then be analyzed via the analysis program. For the control tests, the program assumed that the chambers were well mixed, and that diffusion through the column body was uniform, whether or not the sand screen was in place.

Sand Experiments

The main sand experiments could be run once the set up and model had been validated. Prior to running this set of experiments, the sand had to be dried in an oven and was subsequently sieved to between ASTM 40 and 80 to be sure that none would fall through the screen separating the column body from the bottom chamber and to get rid of clumps. The following experimental procedure was used in running the sand experiments.

1. Close the main column valve and make sure the pressure relief tubing at the top of the column is capped.

2. Remove one of the all thread pieces from the bottom chamber to relieve pressure.

3. Open the valve to the test gas cylinder and set the regulator exit pressure at 50 psig.

4. Let the test gas flow into and through the bottom chamber for 15 minutes. At the conclusion of this time, close the gas cylinder valve and put the all thread piece back into the chamber.

5. Let the column sit for 15 minutes to allow full mixing in the bottom chamber.

6. Set Gaslab to start recording in 30 second intervals for the next 72 hours and open the valve to the column body.

7. At the conclusion of the control test, remove the pressure relief cap and use the air pump to flush out the test gas from the column. If the air from the pump starts to heat noticeably, stop and wait for it to cool back down.

CHAPTER IV

RESULTS AND DISCUSSION

Validation Program

The validation program was run with three different sets of conditions. The first set was just

meant to approximate the expected diffusivity and step sizes to be used in the simulations. The

second set was meant to mimic the measured diffusivity from the control test experiments and the

step sizes used in the simulation while the third set mimicked these for the sand experiment. Once

the program's simulations were run, it would then calculate the percent error for the temperatures

at all of the space step locations within the bar. The maximum percent errors for each simulation

are tabulated below.

Table 4: Validation Program Results

Test	Maximum % Error
Initial Analysis	0.013%
Control Experiment Mimic	0.055%
Sand Experiment Mimic	0.006%

The conditions that each of the analyses were run at are repeated below.

Parameter	Value	Units
Thermal Diffusivity	10^{-6}	m^2/s
Bar Length	1	m
Boundary 1 Temperature	0	°C
Boundary 2 Temperature	0	°C
Temperature (time = 0, x)	$60*\sin(\pi x)$	°C
Simulation Time Step	1	seconds
Simulation Space Step	.01	meters
Total Simulation Time	10000	seconds

Table 6: Validation Program Control Mimic Parameters

Parameter	Value	Units
Thermal Diffusivity	1.4×10^{-5}	m^2/s
Bar Length	1	m
Boundary 1 Temperature	0	°C
Boundary 2 Temperature	0	°C
Temperature (time = 0, x)	$60*\sin(\pi x)$	°C
Simulation Time Step	1	seconds
Simulation Space Step	.0289	meters
Total Simulation Time	1800	seconds

Table 7: Validation Program Sand Mimic Parameters

Parameter	Value	Units
Thermal Diffusivity	4×10^{-7}	m^2/s
Bar Length	1	m
Boundary 1 Temperature	0	°C
Boundary 2 Temperature	0	°C
Temperature (time = 0, x)	$60*\sin(\pi x)$	°C
Simulation Time Step	30	seconds
Simulation Space Step	.01	meters
Total Simulation Time	86400	seconds

Leak Test Experiments

The leak test experiments were done to allow the model to correct for the minor exchange of gas between the column and the surroundings. While minor, it became important over time spans of multiple hours so it needed to be accounted for. These diffusivities represent the diffusivity of

column material necessary to result in the same carbon dioxide loss from the chambers. Said another way, a value of 10^{-6} m^2/s would mean that if the column were packed with a material with a diffusivity of 10^{-6} m^2/s, diffusion of carbon dioxide through the column would result in the same loss of material in the chamber as the leaking would. The data collected for each of the runs is listed below. One day of data was used for each run.

Table 8: Corrective Diffusivity Run Results

	Bottom Corrective Diffusivity		Top Corrective Diffusivity	
	Diffusivity (m^2/s)	SSD	Diffusivity (m^2/s)	SSD
Run 1	4.21E-08	1.20E-09	3.05E-08	9.96E-09
Run 2	4.51E-08	2.77E-09	3.50E-08	2.07E-08
Run 3	2.99E-08	6.78E-09	1.90E-08	3.20E-09
Run 4	3.66E-08	1.46E-08	5.43E-08	2.72E-09
Run 5	5.43E-08	2.72E-09	4.05E-08	2.07E-08
Average	4.14E-08		3.59E-08	

The corrective diffusivity coefficients are nearly three orders of magnitude smaller than the diffusivity of carbon dioxide through air, suggesting that the column leaks have little impact on the carbon dioxide concentrations in the chambers during the control experiments. However, they are only about one order of magnitude smaller than the measured CO_2-sand diffusivity coefficients, which indicates that the leaking played a large role in the measured diffusion behavior exhibited in the sand experiments and had to be accounted for in the concentration data analysis program.

Control Test Experiments

The control test experiments were for validation of the model in conjunction with the experimental set up. Since the diffusivity of carbon dioxide through air is known, the values obtained by these runs can be compared to the known value of 1.4×10^{-5} m^2/s [1][16]. The data from the control test experiments are listed below. While the control test experiments were run for one day each, the carbon dioxide concentrations in the chambers leveled out early in the runs so only thirty minutes of data was used in the concentration data analysis program for each run.

	Diffusivity (m^2/s)	SSD
Run 1	1.38E-05	1.07E-02
Run 2	1.37E-05	8.60E-03
Run 3	1.37E-05	4.09E-03
Average	1.37E-05	

The values obtained from the control test experiments are all the same as the expected value for the diffusivity of carbon dioxide through air, when rounded to the same precision.

A chart of the averaged concentration data from the control experiment series follows below. The error bars on this chart are relatively large despite the consistent diffusivity values because the initial carbon dioxide concentrations varied by nearly 300 ppm.
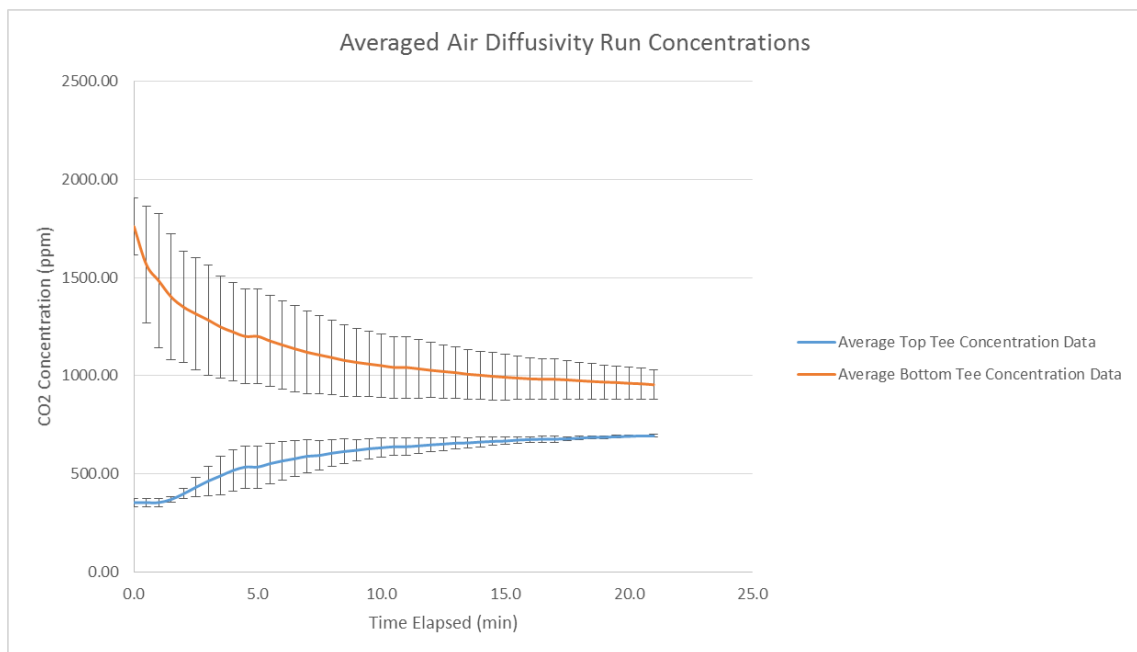
Figure 6: Averaged Air Diffusivity Run Concentrations Plotted over Time

Sand Experiments

Because they were the primary experiments in the series, there were more sand diffusivity experiments run than control or leak experiments, a total of seven runs. Each of the sand experiments were run for three days, and one day of data was used for each.

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Table 10: Sand Test Run Results

	Diffusivity (m^2/s)	SSD
Run 1	3.83E-07	5.56E-06
Run 2	4.06E-07	4.82E-06
Run 3	3.90E-07	7.70E-06
Run 4	3.02E-07	6.06E-06
Run 5	2.96E-07	1.74E-06
Run 6	2.96E-07	1.55E-06
Run 7	3.74E-07	8.11E-06
Average	3.50E-07	
Standard Deviation	4.92E-08	

As expected, the effective diffusivities measured through the sand were much lower than the measured and tabulated values of the diffusivity of carbon dioxide through air, almost by two orders of magnitude. The spread of the sand run diffusivities is similar in magnitude to the spread of the control diffusivities, though this means it is much larger relative to the measured values. The diffusivities range from about $3x10^{-7}$ m^2/s to about $4x10^{-7}$ m^2/s with an average of $3.50x10^{-7}$ m^2/s and a standard deviation of $4.92x10^{-8}$ m^2/s. A chart of the averaged concentration data from the sand experiment series follows below.
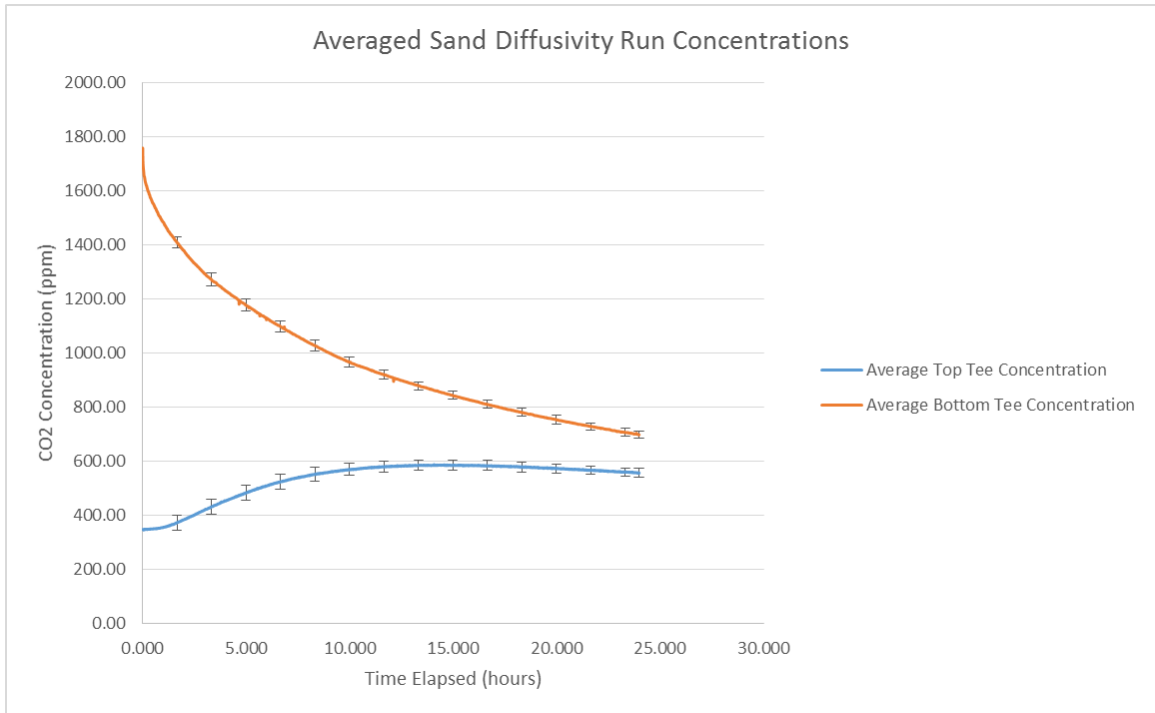
Figure 7: Averaged Sand Diffusivity Run Concentrations Plotted over Time

CHAPTER V

CONCLUSIONS AND FUTURE WORK

Conclusions

The author was able to use the experimental set up described in this work and the concentration

data analysis program to measure the diffusivity of carbon dioxide through sand grains sized

ASTM 40-80. The same type of set up and program should be usable for measuring the

diffusivity of carbon dioxide through different sands, porous media and even gases as well, based

on the repeatability and success of both the sand and air runs.

The use of an optimizer to solve the boundary conditions of the differential equations describing

the diffusion throughout the column was also found to be reasonable based on the control

experiment results. Additionally, the control experiments were also useful in demonstrating that

relatively cheap sensors could be used to take accurate data of carbon dioxide concentrations.

Future Work

A limitation of the work presented thus far is that the diffusion experiments through the sand

were all performed with dry sand. In the field, the sand and soil that leaked carbon dioxide would

be diffusing through would often contain some amount of water, which would have the effect of

slowing the mass transfer of the carbon dioxide through the medium via two mechanisms. The

first of these is diffusion itself, the diffusivity of carbon dioxide through water is much lower than it is in air, so carbon dioxide would diffuse much slower in pores filled with water than it would through pores filled with air. The second mechanism slowing the mass transfer is the dissolution and reaction of carbon dioxide within the water. Before the diffusion of carbon dioxide can reach steady state, the water much first become saturated with carbon dioxide, which reacts to form carbonic acid in equilibrium in the water according to the reactions below;

$$CO_2(g) + H_2O\ (l) \leftrightarrow H_2CO_3$$

$$H_2CO_3 + H_2O\ (l) \leftrightarrow H_3O^+(aq) + HCO_3^-(aq)$$
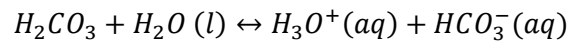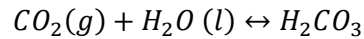
Future experiments could have the sand humidified by passing a heated air stream that has been saturated with water through the sand column. As the humid air passed through the column of sand, the sand would cool it, decreasing the amount of water it can hold and causing some to condense in the sand. At the conclusion of the air injection the column as a whole would cool to ambient temperatures, condensing more of the water in air in the pores. The amount of water deposited in the column could be determined by weighing the system before and after humidification. In such a system, it would be desirable to at least temporarily insulate the column body. If there was a significant heat loss to the environment during the humidification, then even at steady state the temperature at the end away from the humid air injection would be cooler and when the system as a whole cooled there would be a humidity gradient. This gradient would introduce error into the model and make solving for the effective diffusivity difficult so temperature readings would have to be taken to ensure that this was being kept to a minimum.

A major motivator for this project was the possibility of carbon dioxide leaking from direct injection and sequestration sites. Having diffusivity data is very important for having an idea for how quickly leaked carbon dioxide will escape, but modeling of the carbon dioxide diffusion near a leak is necessary for quantifying the amount of carbon dioxide likely to escape from such a leak. With an optimizer and some concentration data from nearby carbon dioxide sensors, a leak

could actually be located in three dimensions with the use of a model for carbon dioxide diffusion

from a leaking site as well.

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[13] Storage of Carbon Dioxide in Geological Formations (Franklin M. Orr Jr.)
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[15] Fundamentals of Carbon Dioxide-Enhanced Oil Recovery- A Supporting Document of the Assessment Methodology for Hydrocarbon Recovery (Mahendra K. Verma)

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APPENDICES

All data and the program used for analysis is available from Dr. Peter Clark.

Control Diffusivity Graphs
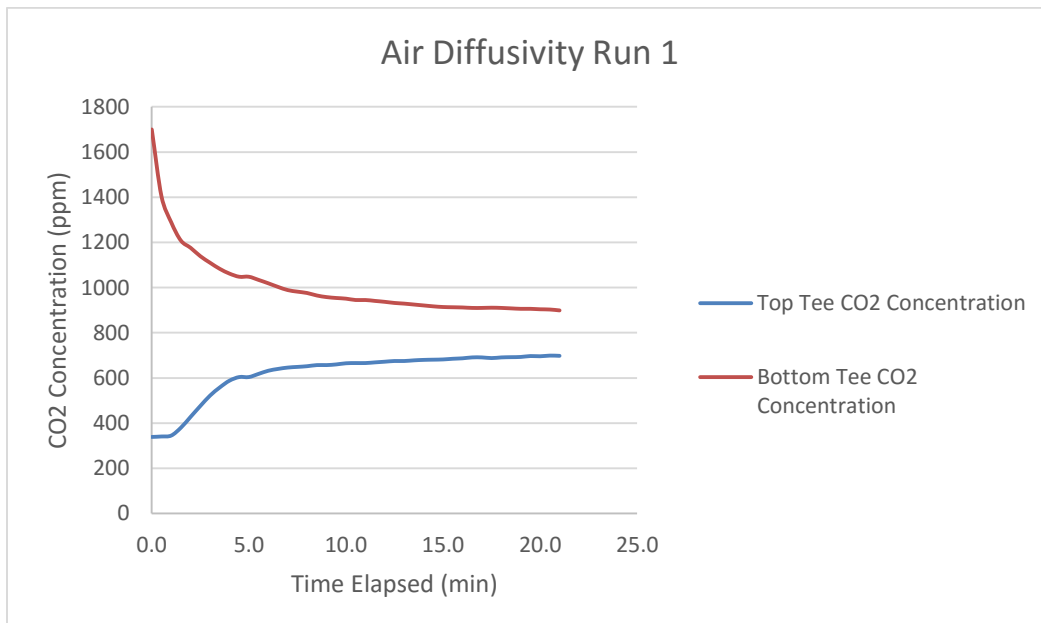
Figure 8: Air Diffusivity Run 1
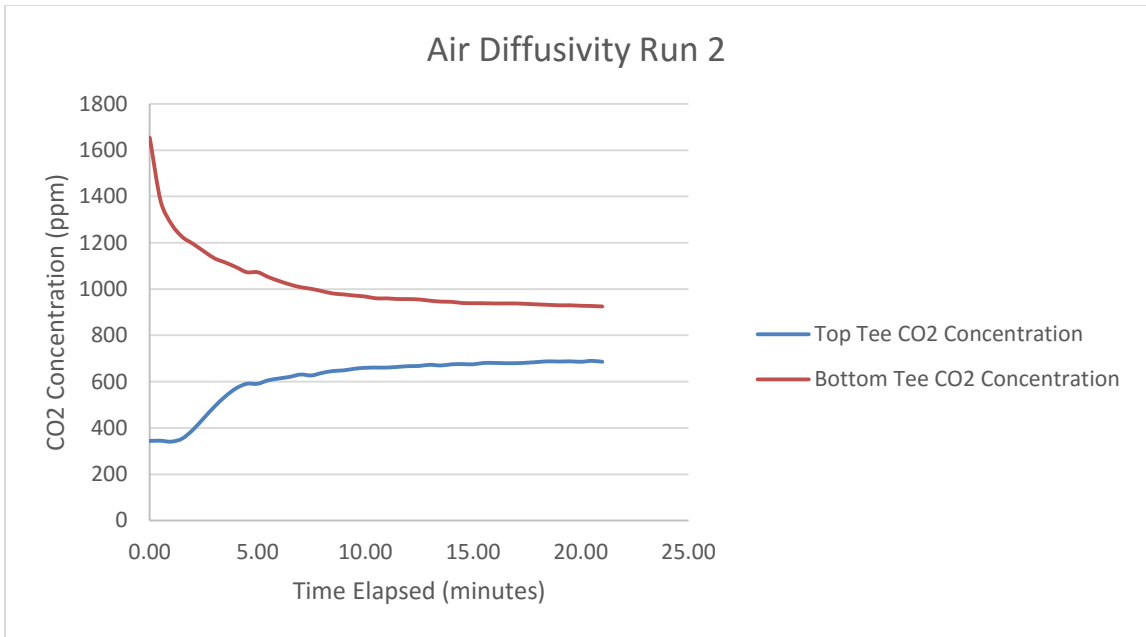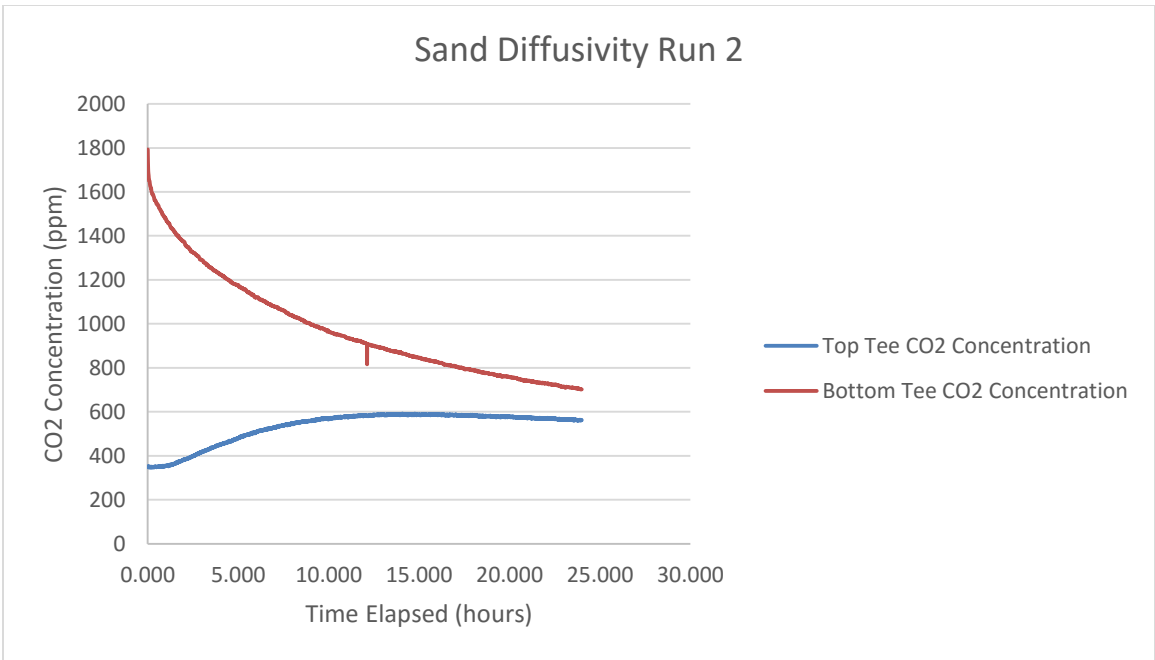
Figure 9: Air Diffusivity Run 2
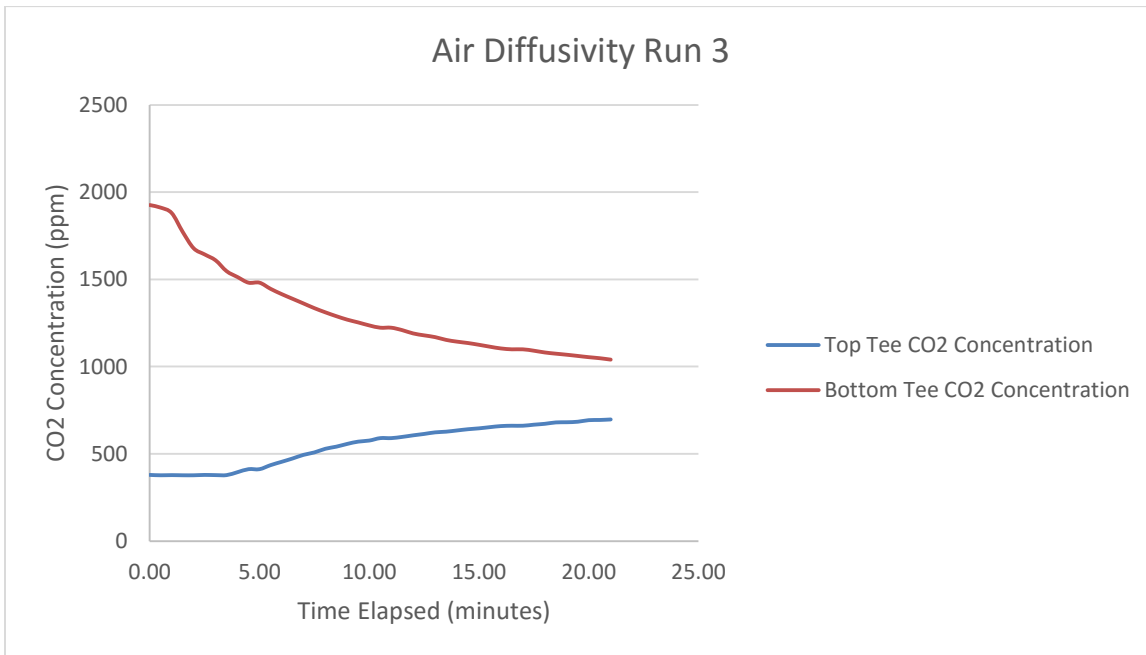
Figure 10: Air Diffusivity Run 3

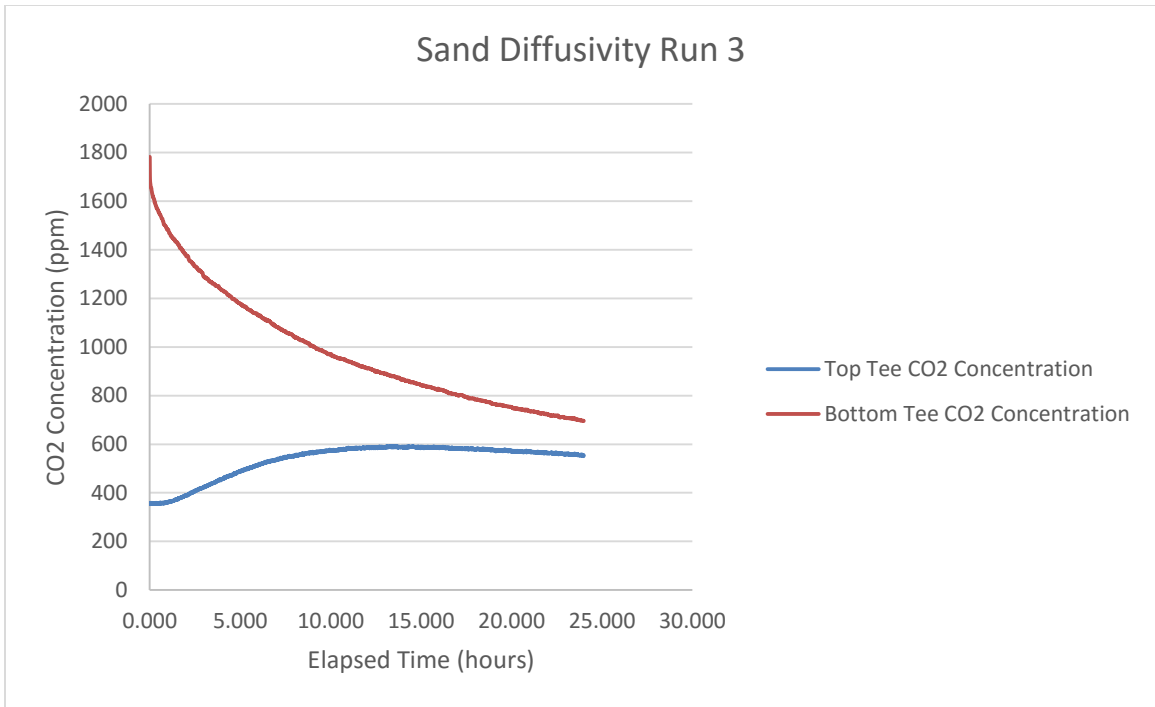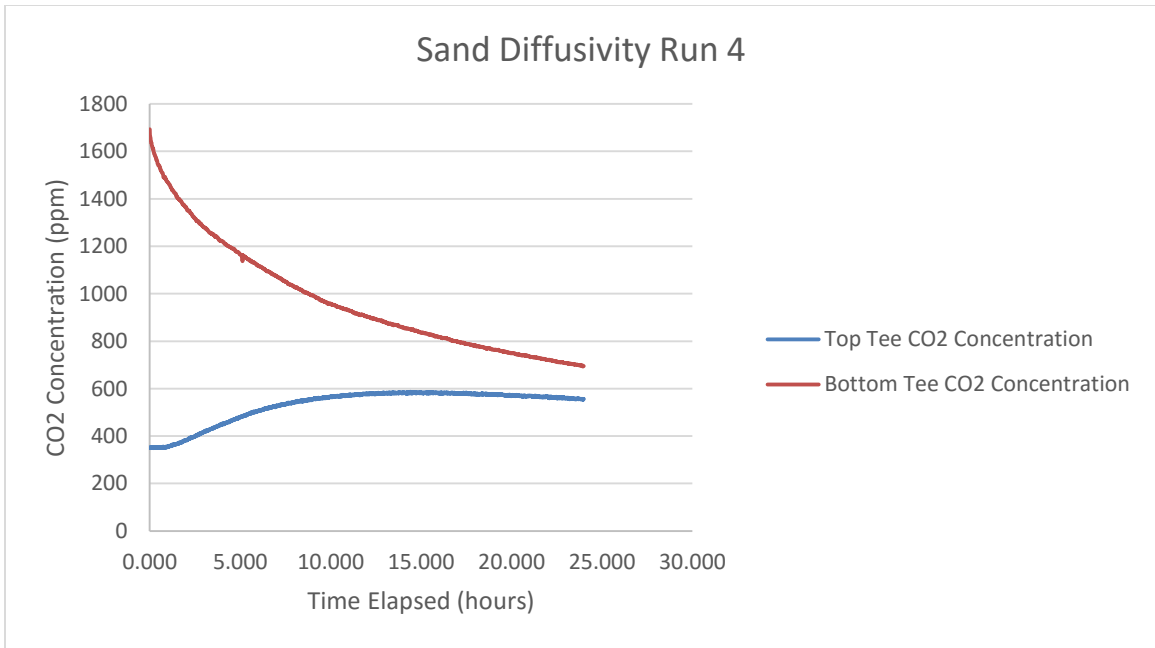Sand Diffusivity Graphs
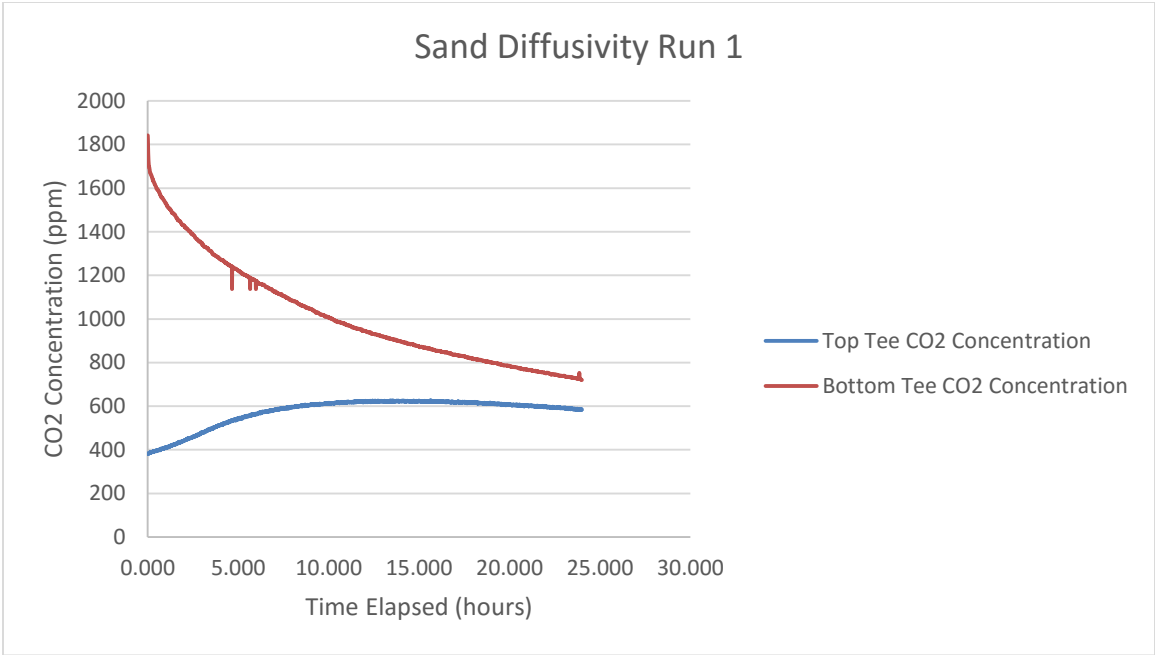
Figure 11: Sand Diffusivity Run 1

Figure 12: Sand Diffusivity Run 2

Figure 13: Sand Diffusivity Run 3
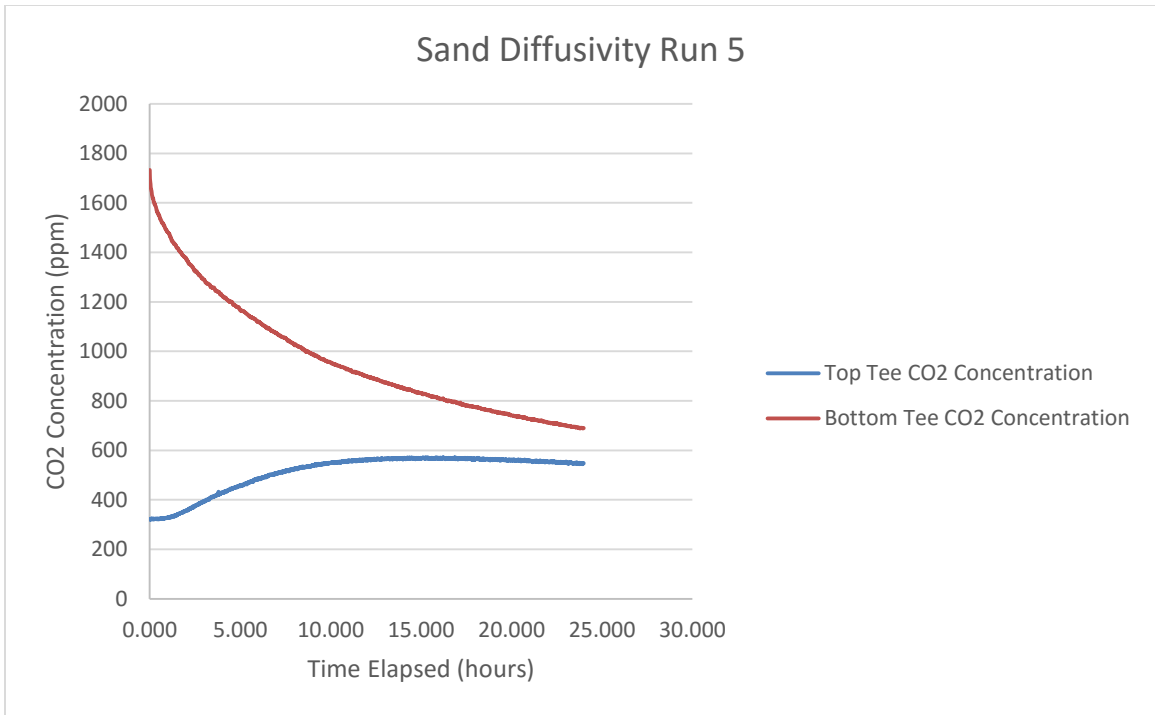

Figure 14: Sand Diffusivity Run 4
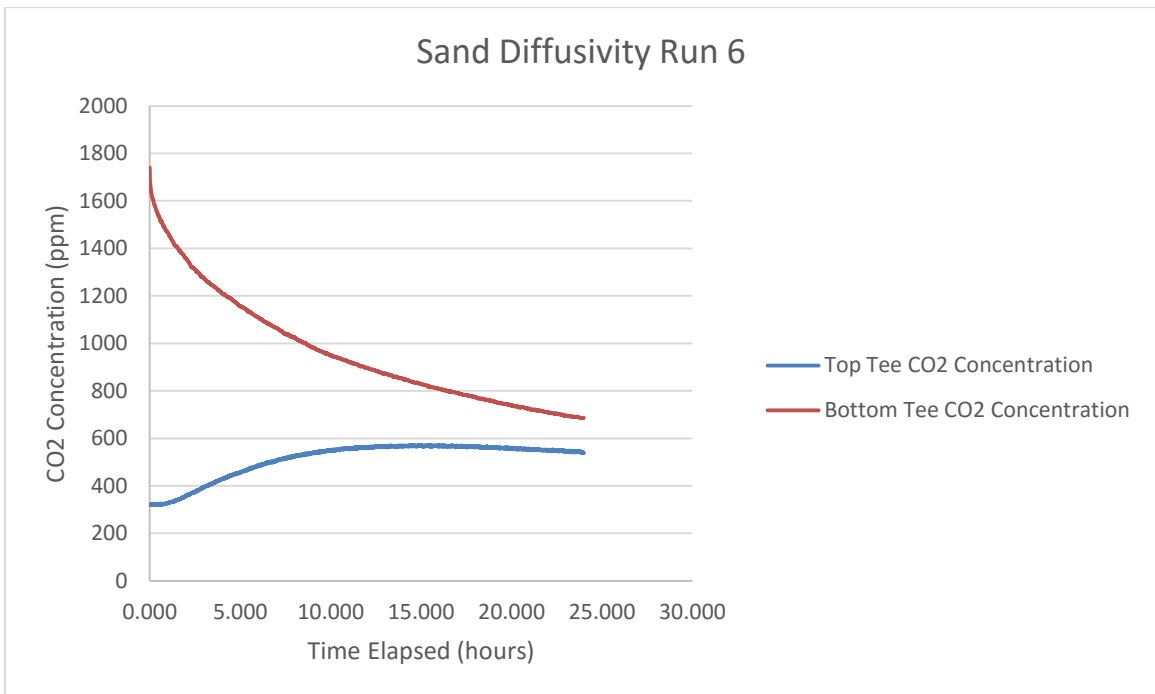
Figure 15: Sand Diffusivity Run 5
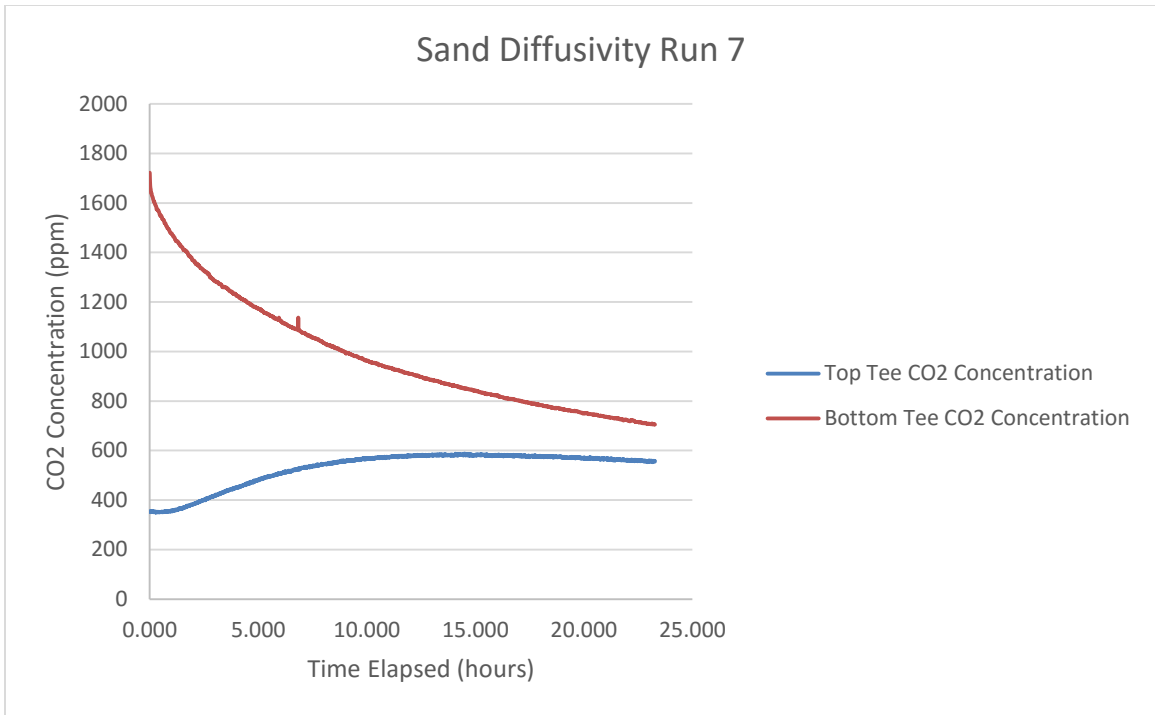

Figure 16: Sand Diffusivity Run 6

Figure 17: Sand Diffusivity Run 7

VITA

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