INVESTIGATION OF REUSE OF COAL FLY ASH TO MITIGATE LANDFILL METHANE

GAS

by

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Abstract

SUSTAINABLE REUSE OF FLY ASH TO MITIGATE LANDFILL METHANE

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Methane (CH_4) is a powerful greenhouse gas (GHG), contributing 32% of current climate forcing (US EPA, 2015). In 2014 the White House released the "Strategy to Cut Methane Emissions" as part of the Climate Action Plan. Landfills are one of the strategy's 4 key sectors, contributing 18% of US methane emissions (US EPA, 2013). Even when landfills capture methane and burn it to produce electricity, around 25% of methane still leaks through landfill covers (US EPA, 2005).

In natural environments, iron oxides, manganese oxides, nitrates, and sulfates have been shown to stimulate microbial anaerobic oxidation of methane (AOM) (Sivan et al., 2014). Adding fly ash, which can contain these components, to the soil of a landfill cover would thus be expected to increase AOM in the lower layers of the cover. The current work is a preliminary study to determine the effect of fly ash on microbial activity of methanotrophs in landfill's final cover.

Two fly ash samples were selected based on their chemical components and adsorption capacity to be mixed with two final cover soil samples. Soil alone and 75% soil- 25% fly ash mixtures were put in batch reactors in contact with a CH_4 and CO_2

mixture, similar to the bio gas produced in landfills. To compare the performance of different samples, the concentration of CH_4 and CO_2 in the reactors was monitored for 40 days, via a gas chromatograph.

The results indicate that adding fly ash to the soil would decrease the performance of microbes to oxidize methane. The concentrations of elements in the fly ash with the potential to oxidize methane (e.g. iron, manganese) were low; in addition, the large fraction of fly ash used (25%) substantially reduced the microbes available for methane oxidation. Fly ash or other wastes with a higher percent of constituents like iron and manganese should be tested, in lower fractions.

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Chapter 1

INTRODUCTION

1.1 Background

1.1.1 Methane emissions from landfills

"Global warming" is a well-known phenomenon today and is one of the most addressed topics in environmental studies in the past decade. The average temperature of Earth's surface has been increasing due to the aggressive extraction and consumption of fossil fuel energy resources in the past century. Simulations suggest that this increase in temperature would accelerate exponentially and irreversibly if it reaches its critical point. They also suggest the fact that earth is reaching its critical point (Hansen, 2008). The greenhouse gases (GHG) are considered to be air pollutants and many laws have been passed by governments to regulate GHG emissions in developed countries.

The most common GHGs generated by human activities are known to be carbon dioxide, methane, nitrous oxides and chlorofluorocarbons (CFCs). Methane is the second-most prevalent GHG after carbon dioxide. Considering the fact that methane's global warming potential (GWP) is over 28 times the GWP of CO_2 in 100-year horizon, makes it more significant (IPCC AR5, 2013). Figure 1-1 below illustrates the contribution of major greenhouse gases.
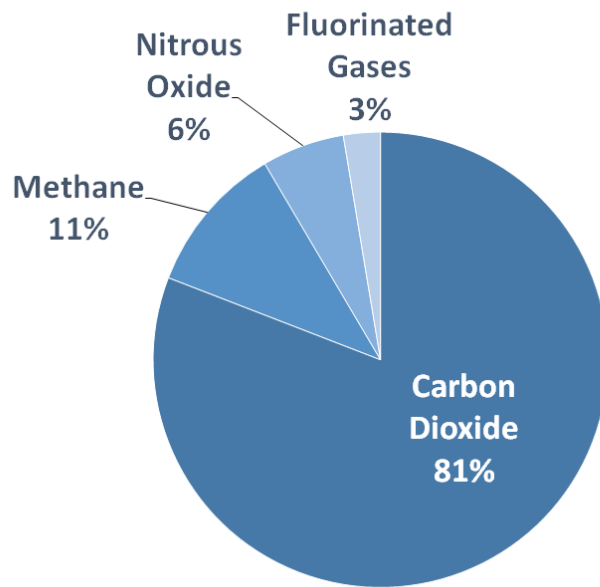
Figure 1-1 US greenhouse gas emissions (EPA, 2017)

Methane is emitted from natural sources such as wetlands, or human activities such as leakage from oil and gas extraction and transportation systems. Methane produced from anaerobic decomposition of organic waste in conventional landfills is mostly captured or oxidized by the microbes in the soil cover. Nonetheless, around 25% of methane generated escapes through the cover (EPA, 2015). That makes landfills the 3rd largest source of methane emissions caused by human activities according to the United States Environmental Protection Agency (EPA, 2013).

Landfills receive non-hazardous waste from homes, businesses and institutions. As landfill waste decomposes, it produces a number of pollutants, including air toxics, volatile organic compounds, carbon dioxide, and methane. Municipal solid waste (MSW) landfills are the third-largest industrial source of methane emissions in the United States,

accounting for 20 percent of methane emissions (EPA, 2014). Methane from landfills can be cost-effectively captured and burned in place of other fossil fuels. Figure 1-2 below shows the methane emissions in U.S. by source for 1990-2014 period.
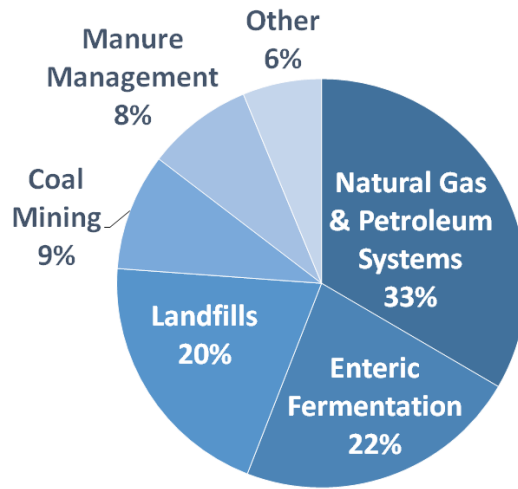
Figure 1-1 US methane emissions by source (EPA, 2017)

Continuing the Obama Administration's commitment to taking action on climate change and protecting public health, EPA is taking actions to further reduce emissions of methane-rich gas from municipal solid waste landfills. Under final rules, new, modified and existing landfills will begin capturing and controlling landfill gas emissions at levels that are one-third lower than current requirements, updating 20-year-old standards for existing landfills (EPA, 2016).

The final rules are expected to reduce methane emissions by an estimated 334,000 tons a year beginning in 2025, which is equivalent to reducing 8.2 million metric

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tons of carbon dioxide. EPA estimates the climate benefits of the combined rules at $512 million in 2025 or more than $8 for every dollar spent to comply (EPA, 2016).

In addition, EPA's Landfill Methane Outreach Program (LMOP) provides landfill owners and operators a suite of tools and technical resources to facilitate development of landfill gas energy projects. Over the last 20 years, LMOP-assisted projects have reduced and avoided more than 345 million metric tons of carbon dioxide equivalents (EPA, 2016).

1.1.2 Coal Ash Waste

Despite all the efforts to find sustainable alternatives to produce electricity, fossil fuel combustion contributes 67% of the United States electricity demand. About 40% of that energy comes from coal combustion, leaving 110 million tons of unburned solid residues every year. Half of that amount is currently being re-used and the other half is being disposed (US EIA, 2014).

On-site deposition and landfilling are the common ways to dispose of fly ash. When fly ash is stored in bulk, it is usually wet rather than dry in order to minimize fugitive particles. Fly ash has a high potential to cause groundwater contamination since coal has a trace level of elements such as arsenic, barium, chromium, thallium and mercury, and after combustion, the concentration of these elements would increase. Wet storage of fly ash requires leachate control to prevent ground water contamination (American Coal Ash Association, 2015). Moreover, despite the fact that fly ash impoundments are stable for a long period, any breach of their dams or bunds are rapid and massive. In December 2008, an embankment of wet fly ash storage at Kingston Fossil plant in Tennessee

collapsed, causing major release of fly ash and contaminated the Emory River. Homes in the nearby community were destroyed and the clean-up cost was estimated to be $1.2 billion (Associated Press, December 2014).

The Coal Ash Surface Impoundment Integrity Assessment Program was a comprehensive evaluation done by EPA to evaluate the condition and safety of coal ash ponds in the United States. In March 2009, EPA began assessing all coal ash surface impoundments and by 2012 had concluded one of the largest targeted field assessments ever conducted by EPA.

EPA set national regulations to provide for the safe disposal of coal combustion residuals from coal-fired power plants. The rule establishes technical requirements for landfills and surface impoundments under Subtitle D of the Resource Conservation and Recovery Act (RCRA), the nation's primary law for regulating solid waste. EPA is also establishing recordkeeping and reporting requirements under this final rule, including the online posting of annual groundwater monitoring and corrective action reports, coal combustion residual fugitive dust control plans and closure completion notifications.

"Beneficial use" is the recycling or reuse of coal ash as an alternative for disposal. For example, coal ash is an important ingredient in the manufacture of concrete and wallboard, and EPA supports the responsible use of coal ash in this manner. This final rule supports the responsible recycling of coal ash by distinguishing beneficial use from disposal.

Beneficial use of coal ash can produce positive environmental, economic and performance benefits such as reduced use of virgin resources, lower greenhouse gas

emissions, reduced cost of coal ash disposal, and improved strength and durability of materials.

As of 2012, according to the American Coal Ash Association (ACAA) data, approximately 50 percent of the CCRs beneficially used on an annual basis falls into two categories: fly ash used as a direct substitute for Portland cement during the production of concrete (referred to as "fly ash concrete") and FGD gypsum used as a replacement for mined gypsum in wallboard (referred to as "FGD gypsum wallboard") during use by the consumer.

The beneficial use criteria set by EPA are as follows:

1. "The CCR must provide a functional benefit;

2. The CCR must substitute for the use of a virgin material, conserving natural resources that would otherwise need to be obtained through practices such as extraction;

3. The use of CCRs must meet relevant product specifications, regulatory standards, or design standards when available, and when such standards are not available, CCRs are not used in excess quantities;

4. When unencapsulated use of CCRs involves on site deposition of 12,400 tons or more in non-roadway applications, the user must demonstrate and keep records, and provide such documentation upon request, that environmental releases to

ground water, surface water, soil and air are comparable to or lower than those from analogous products made without CCRs, or that environmental releases to ground water, surface water, soil and air will be at or below relevant regulatory and health-based benchmarks for human and ecological receptors during use."

Fly ash disposal can take massive land and monitoring costs. The adverse economic and environmental impacts, increasing disposal costs, land reuse and saving natural resources have been motivating the industry to find new ways to safely re-use fly ash.

1.2 Research Goals and Objectives

The final cover in landfill is a multi-layer compacted soil which is responsible for reducing the amount of storm water from entering the landfill, erosion and migration of landfill gases. USEPA requires landfills to implement a two-foot layer of soil, compacted to a point to reach permeability of less than 10^{-5} cm/sec. Methane oxidizer organisms in the cover soil on average mitigate 36% of methane passing through (Chanton, 2009).

Iron oxides, nitrate and sulfate have been shown to promote anaerobic activity of methanotrophs in natural environments (Sivan et al., 2014). Adding fly ash to cover soil, which contains a considerable amount of these components, is expected to promote methane oxidation. Especially in lower layers of the cover soil where limited diffusion of oxygen leads to anaerobic conditions, methanotrophs could use sulfate as electron donor to oxidize methane. Also the metal compounds in fly ash could help microbes to adsorb methane by attaching to their membranes.

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Adding fly ash to soil can modify the texture of final cover. Fine grains of fly ash, especially cementitious fly ash, can fill in the porosity of soil and help reach lower permeability. Fine particles can also increase the adsorption capacity of soil to capture methane.

The goal of this project is to evaluate the enhancement of methane mitigation in final cover soil by the added fly ash. Specific objectives were:

1. To determine the chemical composition and adsorption capacity of different 5 fly ash samples in order to find the best candidates for soil mixtures,

2. To conduct batch tests with fly ash/soil mixtures to determine the best absorber of methane.

The use of fly ash in land fill cover would be a sustainable use of fly ash which also reduces its disposal and helps reducing methane emissions from landfills.

Chapter 2

Literature Review

2.1 Introduction

This chapter will demonstrate the characteristics of fly ash and its applications, along with methane oxidation in soils and methanotrophic activity.

2.2 Fly Ash and Its Applications

Fly ash is one of the coal combustion residuals. Composed of very fine and predominantly spherical particles, they are rich in silica and amorphous. Fly ash is particulates captured from exhaust gas by electrostatic precipitators and bag houses of coal-fired power plants. Figure 2-1 is an image of fly ash particles taken by an electron microscope.
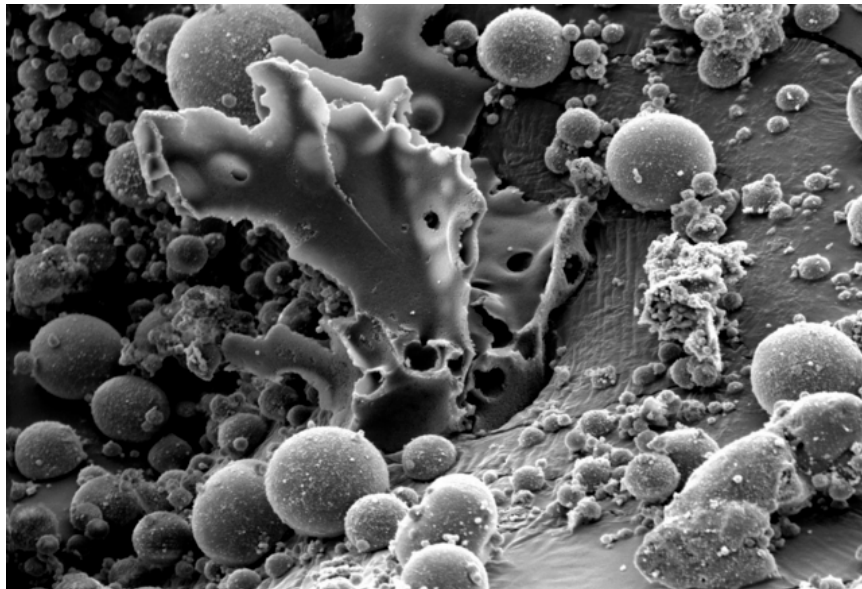
Figure 2-1 Scanning electron microscope image of fly ash grains

Fly ash's composition is mainly based on the source of coal and characteristics of the boiler/combustion process. However, a significant amount of silicon dioxide (SO_2), aluminum oxide (Al_2O_3) and calcium oxide (CaO) can be found in different types of fly ash (Snellings et al., 2012). The main classification of fly ash separates them into two classes. Class F fly ash is typically a product of burning harder, older anthracite and bituminous coal. This fly ash has low or no cementitious value and contains less than 7% lime. The glassy silica and alumina of class F fly ash requires a cementing agent or hydrate lime to react and produce cementitious compounds.

Class C fly ash is typically produced by burning younger lignite or sub-bituminous coals. Class C has self-cementing properties, which means in contact with water, Class C fly ash hardens and gets stronger over time. Alkali and sulfate (SO_4) contents are higher in Class C fly ashes.

On-site deposition and landfilling are the common way to dispose of fly ash. When fly ash is stored in bulk, it is usually wet rather than dry in order to minimize fugitive particles. Fly ash has a high potential to cause groundwater contamination since coal has a trace level of elements such as arsenic, barium, chromium, thallium and mercury, and after combustion, the concentration of these elements would increase (Research Triangle Park, 2017). Wet storage of fly ash requires leachate control to prevent groundwater contamination.

The adverse economic and environmental impacts, increasing disposal costs, land reuse and saving natural resources have been motivating the industry to find new ways to utilize fly ash. Figure 2-2 shows different uses of fly ash.
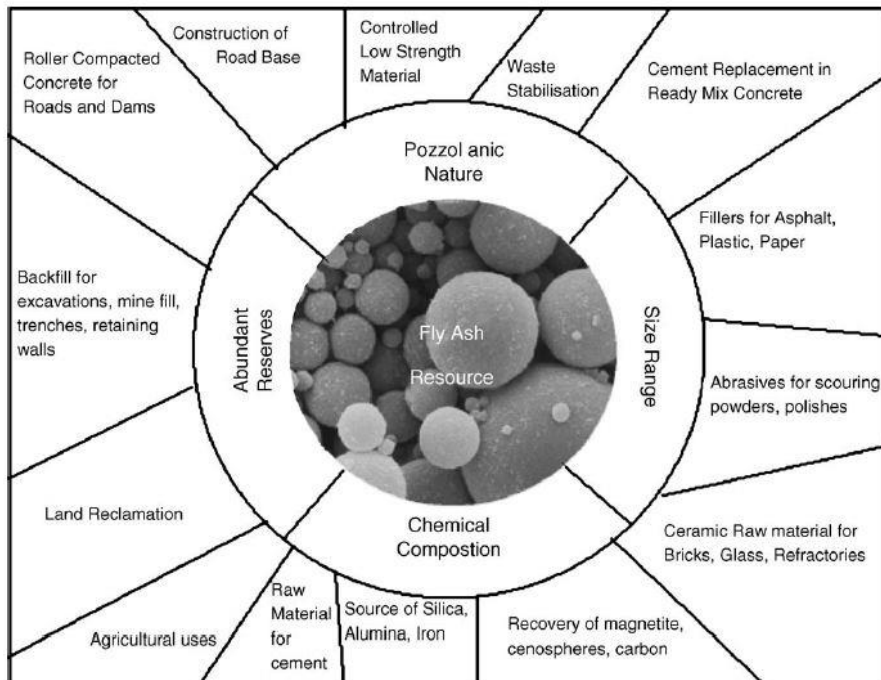
Figure 2-2 Uses of fly ash (Wang et al., 2006)

In April 2015, EPA's final CCR disposal rule which reaffirms EPA's determination for "beneficial use" of coal ash to be distinguished from coal ash disposal. The beneficial use of fly ash is defined by EPA as "*the reuse in a product that provides a functional benefit, replaces a product made from virgin raw materials, conserves natural resources and meets product specifications and industry standards. Beneficial use of waste products can contribute to a sustainable future by reducing production costs, reducing energy consumption and greenhouse gasses.*"

According to the EPA, beneficial uses of fly ash include serving as a raw material in concrete, grout and cement or as a fill material in stabilization projects and road beds.

Bottom ash is generally just used as fill or snow control on roads. Around 43% of fly ash in the USA is currently reused with the largest use by far being the replacement of Portland cement (ACAA, 2014).

Traditional stonework takes significant volumes of energy to produce; therefore, concrete and brick-making are some of the biggest sources of greenhouse gasses. Clay bricks are produced in a kiln and fired at 2000° F for 3-5 days (Brick Industry Association, 2006). The kilns are generally left running continuously even when no bricks are being produced due to the difficulty in getting the temperatures up to optimum levels. Portland cement is also a fired material and releases additional carbon emissions from the calcination of the limestone feedstock. According to NIST (National Institute of Standards and Technology), the carbon footprint for a cubic yard of fired clay brick is 991 pounds and 572 pounds for concrete brick (Bruke et al., 2009). Figure 2-3 illustrates the relative carbon dioxide emissions from brick production using clay, concrete and fly ash.

Relative CO₂ Emissions Associated With Brick Production
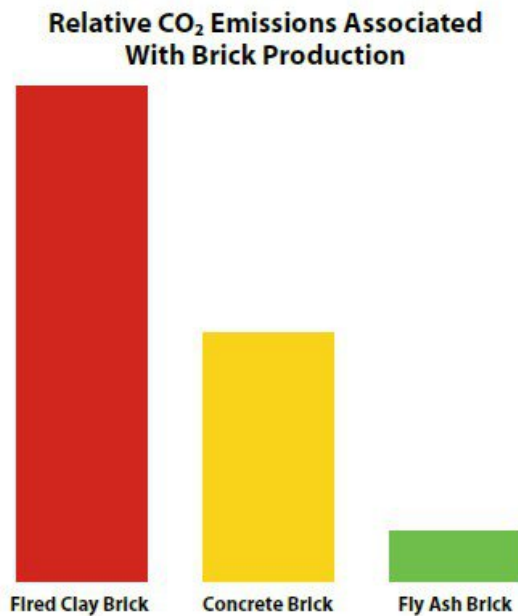
Figure 2-3 Relative CO_2 emissions associated with brick production

Critics believe that recycling of fly ash in concrete building materials is dangerous because it offers weaker structural capability and may result in indoor air contamination due to leaching chemicals or reactions with other materials. Differences in the chemical composition of fly ash from different sources may compound the problem by making it difficult to assure the proper strength of the final concrete products (EPA, 2015).

The characteristics of fly ash such as porosity, fine-grained particles, high surface area and water holding capacity, make it suitable to be used as an adsorbent. Activated carbon is the prevalent adsorbent used to treat flue gas containing SO_x, NO_x, VOCs and mercury but is very costly for large scale applications. Fly ash is a cheap alternative for activated carbon, especially for large scale environmental remediation

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uses. A study done on fly ash suggests that by adding calcium hydroxide to fly ash, it can be used for desulphurization processes (Davini, 2002).

2.3 Methanotrophs and Aerobic Methane Oxidation in Soils

Methanotrophs are single-cell organisms that utilize methane as their carbon source. They can grow aerobically and anaerobically and depended on single-carbon compounds. They can be found in environments where methane is produced. Their common habitat is soils but they can also be found in oceans, mud, rice paddies and landfills.

Methanotrophs are divided in to three main groups. Type I and Type X are proteobacteria which employ the ribulose monophosphate pathway to assimilate formaldehyde, whereas type II methanotrophs employ the serine pathway for formaldehyde assimilation. Type I methanotrophs are dominant in environments with limiting methane and relatively high levels of nitrogen and copper. Type II bacteria are favored in environments with low methane and oxygen levels with limiting concentration of nitrogen or copper (Hanson, 1996). Figures 2-4 and 2-5 show RuMP and serine Pathways for type I and type II methanotrophs.
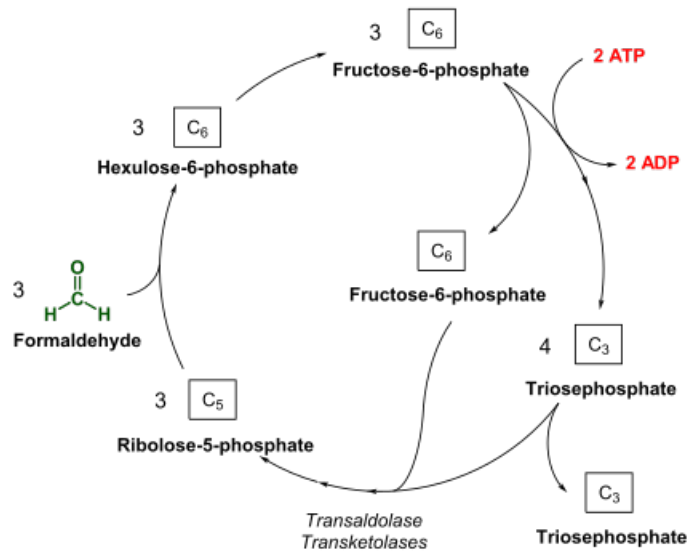
Figure 2-4 RuMP pathway in type I methanotrophs
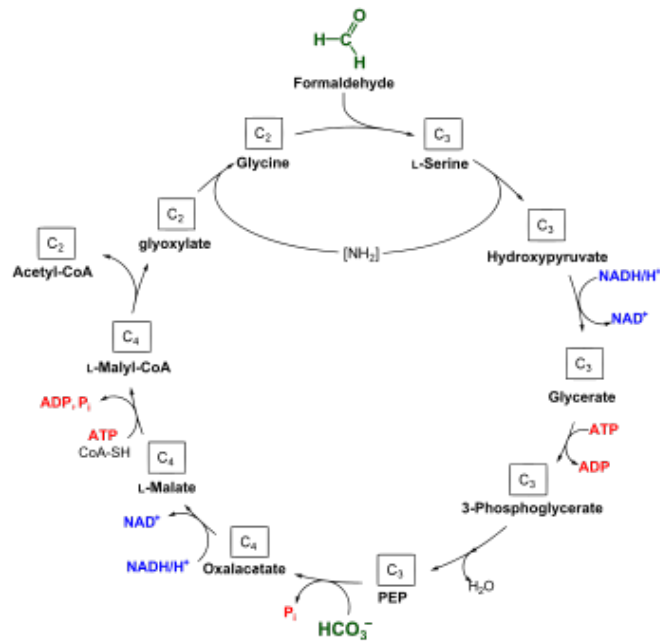
Figure 2-5 Serine pathway in type II methanotrophs

Microbial activity depends on many factors, but one of the most important factors is moisture. Moisture helps to maintain the microbial activity in the landfill covers. However, excessive moisture limits the transport of CH_4 through the cover (Yamini and Reddy, 2014). An optimum soil moisture content of 10-20% w/w is required to maintain a balanced environment in the cover soil for aerobic CH_4 oxidation. Boeckx et al. (1996) reported that the optimal microbial activity for aerobic methane oxidation occurs in water content ranged between 15.6 and 18.8% w/w. Park et al. (2009) reported the optimum moisture content for methane oxidation under aerobic conditions was in the range of 10-15% by weight.

The other important factor is temperature. For methanotrophs, the methane oxidation rate typically increases with an increase in temperature. Lower temperatures cause microbial activity to cease, which inhibits CH_4 oxidation (Borjesson and Svensson, 1997). Most methanotrophs are mesophylls, meaning they can grow under moderate temperature ranges from 25 to 35 °C, although Type I methanotrophs can oxidize methane at lower temperatures ranging from 2 to 10 °C. Various studies have reported the optimum operating temperature ranging from 25-35 °C. Czepiel et al. (1996) reported that oxidation stops when the temperature reaches at 45°C (Spokas and Bogner, 2011; Park et al., 2009).

The optimum soil pH range for methane oxidation is 5.5-8.5. Since methanotrophs have the capacity to adapt to a wide range of pH values, this is not a major limiting factor for microbial methane oxidation (Scheutz et al., 2009a, b).

2.4 Anaerobic Methane Oxidation

Investigations in marine environments have revealed that methane can be oxidized anaerobically by collaboration of methane oxidizing archaea and sulfate-reducing bacteria (Knittel et al., 2009) Anaerobic oxidation of methane (AOM) mainly occurs in anoxic sediments. The exact mechanism of methane oxidation under anaerobic conditions is still a topic of debate, but the most accepted theory is that the archaea use the "reversed methanogenesis" pathway to produce carbon dioxide (Scheller et al., 2010). This intermediate product is then used by the sulfate-reducing bacteria to gain energy from the reduction of sulfate to hydrogen sulfide. The overall reaction is:

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$$

This reaction is not, however, desirable in a landfill cover because HS^- leads to hydrogen sulfide, which is an odor-causing gas.

Recently, a new bacterium (*Candidatus Methylomirabilis oxyfera*) was identified that can couple the anaerobic oxidation of methane to nitrite reduction without the need for a syntrophic partner. Based on the studies of Ettwig et al. (2010), it is believed that *M. oxyfera* oxidizes methane anaerobically by utilizing the oxygen produced internally from the splitting of nitric oxide into nitrogen and oxygen gas.

One way to reduce methane emissions is to inhibit methane fermentation. Methane fermentation is a biochemical process which converts hydrocarbons into methane and carbon dioxide under anaerobic conditions. The process is a result of consecutive biochemical breakdown of polymers in which a variety of microorganisms

including hydrolytic bacteria, fermentative microbes (acidogens), acetogen microbes and methanogens cooperate to make the end products. At the last stage of this process, methanogenic bacteria convert H_2, CO_2 and acetate to CH_4 and CO_2, according to:

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2H_2O$$

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$$
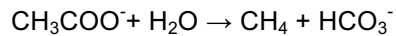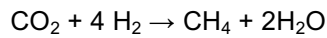
In the first reaction, CO_2 works as an electron acceptor. Previous studies suggest that the presence of a more favorable electron acceptor such as Fe^{3+}, NO_3^- and SO_4^{2-} could outcompete CO_2 and decrease methane production (Lovely et al., 2004). The electron acceptors can also oxidize methane to CO_2; example reactions are shown below.

$$CH_4 + SO_4^{2-} + 2H^+ \rightarrow H_2S + CO_2 + 2H_2O$$

$$CH_4 + 8\ Fe(OH)_3 + 15\ H^+ \rightarrow HCO_3^- + 8\ Fe^{2+} + 21\ H_2O$$
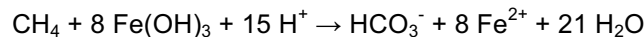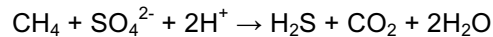
It has been recognized that utilizing iron oxide in submerged conditions would control the production of organic acids (Asami and Takai, 1970) and CH_4 (Watanabe and Kimura, 1999). However, applying amorphous iron oxide may not be feasible due its high cost. Utilizing industrial by-products which contain these electron acceptors are the best alternative, since they are economically feasible and could also be good soil amendments for agricultural purposes. Figure 2-6 presents the results from a study on the effect of industrial by-products on methane emissions during rice cultivation (Ali et al., 2009).
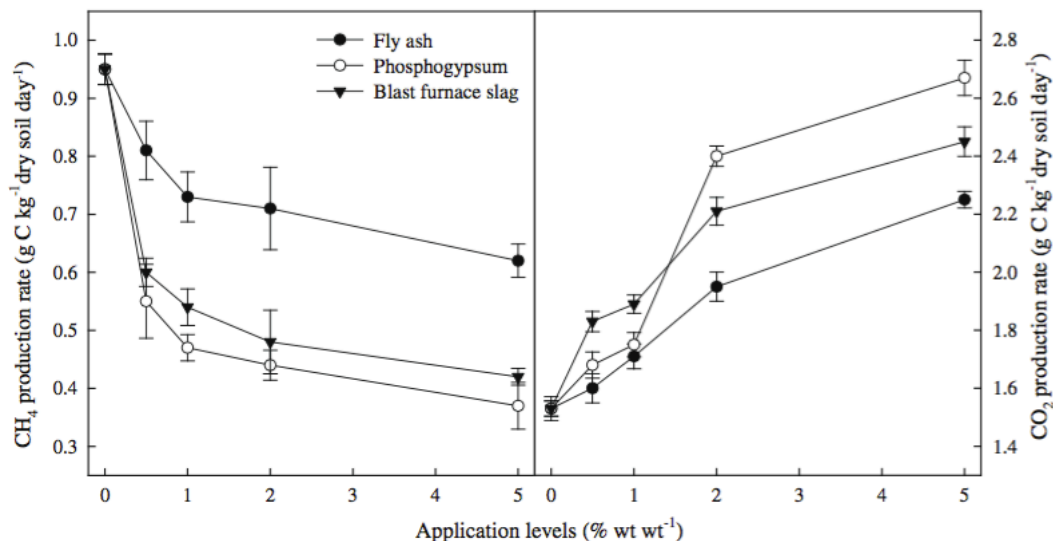
Figure 2-6 CH_4 and CO_2 production rates with different levels of soil amendments applied

Blast furnace slag, phosphogypsum and fly ash are three industrial by-products containing considerable amounts of iron oxide, sulfate and nitrates. In the research by Ali et al., these amendments were applied at different rates to the rice paddies. It was observed that CH_4 production rates were significantly decreased, while CO_2 production rates linearly increased, with the increasing levels of soil amendments applied. Although the total seasonal CH_4 flux reduced by fly ash was lesser compared to blast slag and phosphogypsum, it still reduced the flux by 20% with adding 10 Mg of fly ash per hour, while increased rice yields by 17% over the control sample (Ali et al., 2009).

Chapter 3

Methodology

3.1 Preliminary Tests

Prior to the main experiment, several tests were conducted to identify the composition of samples and their adsorption behavior in the presence of methane and carbon dioxide gases. The samples used for the experiment include two soil samples designated as S1 and S2, two class C fly ash samples designated as C1 and C2 and three fly ash samples which will be referred to as F1, F2 and F3. The soil samples were collected from different intermediate cover soils in the City of Denton Landfill. The fly ash samples were obtained from 5 different coal-fired plants, which will not be identified at the request of the power companies.

3.1.1 Sample Composition

The composition of samples was identified using Electron Spectroscopy for Chemical Analysis (ESCA), also called X-ray Photoelectron Spectroscopy (XPS). The ESCA data were acquired from an analyzed area having a diameter of ca. 1 mm using a monochromatic Al Kα x-ray source. Low energy resolution survey scans were obtained from each sample to determine what elements were present. The atomic concentration of these elements and their local chemistries were determined from higher energy resolution multiplex scans. The analysis was done by Innovatech Labs, Inc.

Results from ESCA were used to identify the amount of iron oxide and sulfate. As discussed in Chapter 2, iron oxide and sulfate could potentially favor the anaerobic oxidation of methane. Also comparing XPS results for samples before and after their

exposure to methane gas could be used to identify the compounds which were utilized in the oxidation process, along with the extent of their utilization.

3.1.2 Surface Area Analysis

The specific surface area of fly ash samples for methane and carbon dioxide was evaluated using the Brunauer–Emmett–Teller (BET) method. The BET test is used to measure the available surface area of solids for physical adsorption of gas molecules. BET also provides an adsorption isotherm plot which indicates the adsorption capacity of solid sample for a specific gas at different pressures, which includes multi-layer adsorption. The analyses were done in the Center for Renewable Energy Science and Technology (CREST) lab at UTA.

The surface area of fly ash samples was measured using Mircromeritics, TriStar ll Plus by CO_2 and CH_4 at 273.6K as shown in Figure 3-1. Prior to analysis, each sample (about 0.5 g) was placed in an analysis tube and degassed at 290°C for 24h to remove any adsorbed species. After degassing, the sample was transferred to the analysis station, where it was cooled in ice-water bath at 273.6K. High purity CH_4 and CO_2 gases were used as the adsorbate in the analysis. N_2 was also used as backfill gas. Each sample was tested with high purity (99.9%) methane and carbon dioxide.
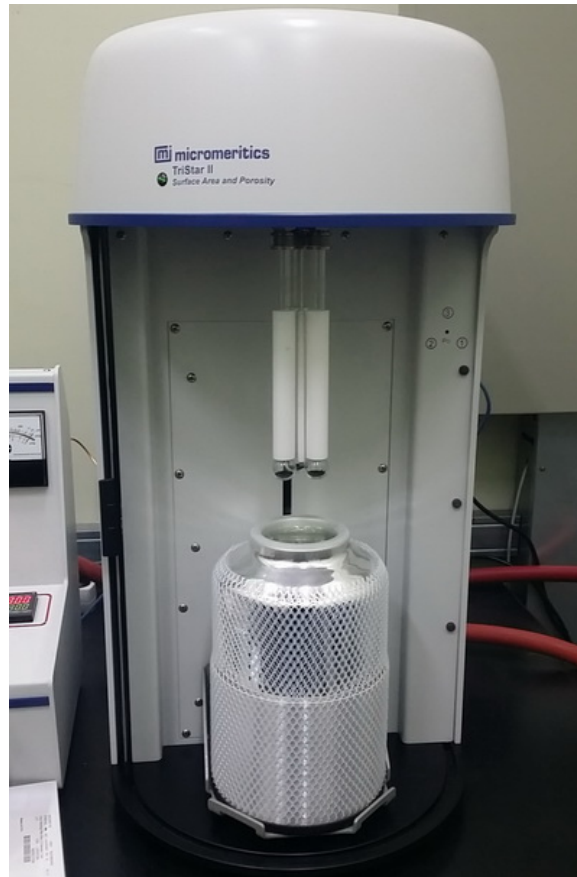
Figure 3-1 TriStar II Mircromeritics Surface Area Analyzer

3.2 Experimental Design

A laboratory study was conducted to evaluate the performance of soil and fly ash mixtures to oxidize methane. The kinetics of methane oxidation was measured for different samples by monitoring the concentration of methane and carbon dioxide in a batch system. The other alternative, a continuous-flow system, was not used due to difficulties in maintaining constant conditions and leakage. A batch system is simpler to

operate. A continuous system also needs a humidifier to replace the water vapor escaping from the system in order to maintain the moisture content of the sample.

Soil samples S1 and S2, which were collected from the Denton Landfill, were used to represent the landfill's final cover. The samples were taken from intermediate cover soil where soil had been exposed to methane, in order to obtain samples with methanotrophic microbes. S1 was taken from a cell with sandy clay cover and S2 was taken from a cell with clay cover soil. Fly ash samples C1 and F3 were chosen to be utilized in the experiment. Fly ash selection was based on the results from preliminary test results, which will be discussed in Chapter 4.

The amount of fly ash added to soil were determined by two factors. Fly ash content should be enough to increase the iron and sulfur content of the samples. However, in case of Class C fly ash, the excessive use of fly ash would increase the calcium carbonate ($CaCO_3$) content of the mixture. A high amount of $CaCO_3$ increases the self-cementing property of the mixture, which would result in fractures in the landfill's final cover. Table 3-1 shows the combination of materials used in each reactor.

Table 3-1 Experimental design

Reactor	Composition
1	S1
2	S2
3	75% S1 + 25% C1
4	75% S2 + 25% C1
5	75% S1 + 25% F3
6	75% S2 + 25% F3

The total dry weight of sample used in each reactor was 40 g in order to maintain the sample to gas ratio of 1/11 from previous studies (Kim et al., 2016). Also, 5 ml of water was added to increase the moisture content of samples to slightly over 10% and in the typical range for landfill final covers (10-15 %).

To start the experiment, each reactor was purged for 5 minutes with a mixture of methane and carbon dioxide gases. The feed gas consisted of 50% methane and 50% carbon dioxide, which is a mixture similar to landfill gas.

3.3 Setup

The reactors were made from 15 oz. PVC bottles with a self-sealing lid (McMaster-Carr part number 43045T53). Among common polymers, PVC has the lowest gas permeability coefficient (Stanislav et al., 2007). In addition, PVC is chemically inert in standard temperature and pressure (STP) conditions and will not react with methane.

The samples were flattened at the bottom of reactors in order to achieve a uniform thin layer. This configuration was used to avoid gas diffusion limitations. In case of limited diffusion, the adsorption process would be limited by the flux of gas traveling through the sample, which leads to zero-order kinetics. However, the kinetics of a non-limited adsorption process is first-order, similar to what is expected from microbial activity. Minimizing diffusion would simplify the data analysis. However, if the rate of adsorption and chemical reaction surpass the rate of diffusion, the kinetics of the diffusion process would control the overall rate. In this case, evaluating the kinetics of other processes would be impossible. Figure 3-2 shows one of the reactors used in the experiment.
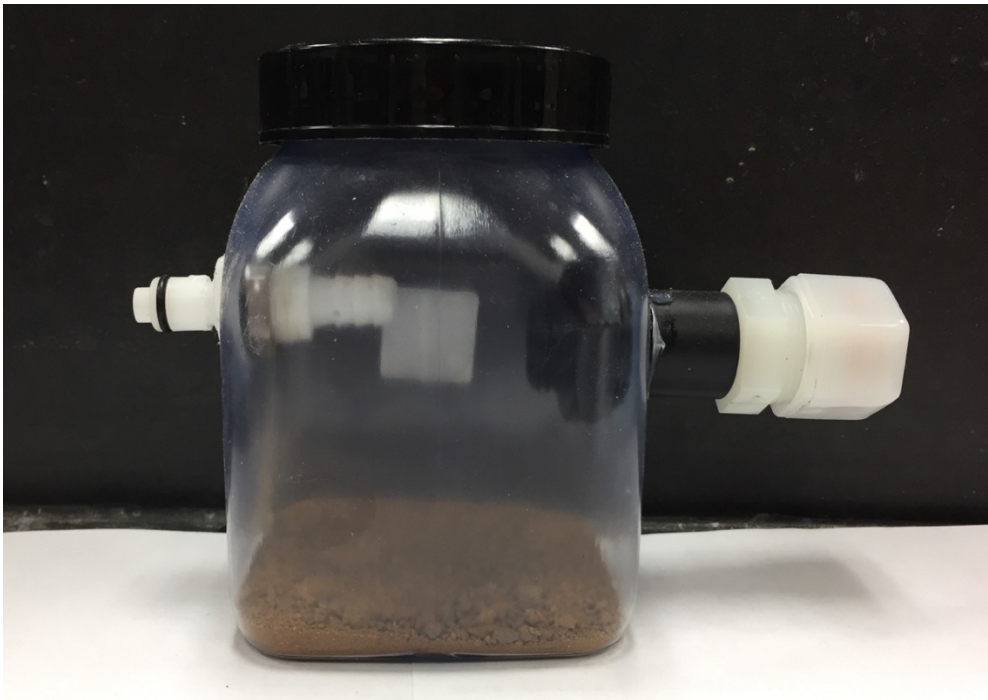
Figure 3-1 Batch reactor setup

Each reactor has two ports on the side walls. One port was installed for sample collection. A half an inch diameter compression tube fitting was used to hold the septa. The compression tube fitting (McMaster-Carr 50775K337) was then attached to a through-wall fitting (McMaster-Carr 8674T56) in order to be installed on reactor's wall. Figure 3-3 and 3-4 show through-wall fitting, and the compression tube fitting. Figure 3-5 show how the two fittings were coupled.
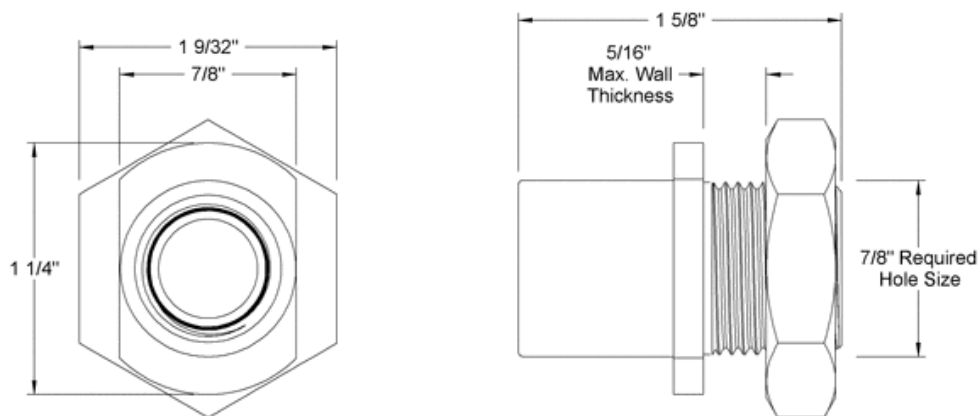
Figure 3-3 Through-wall fitting
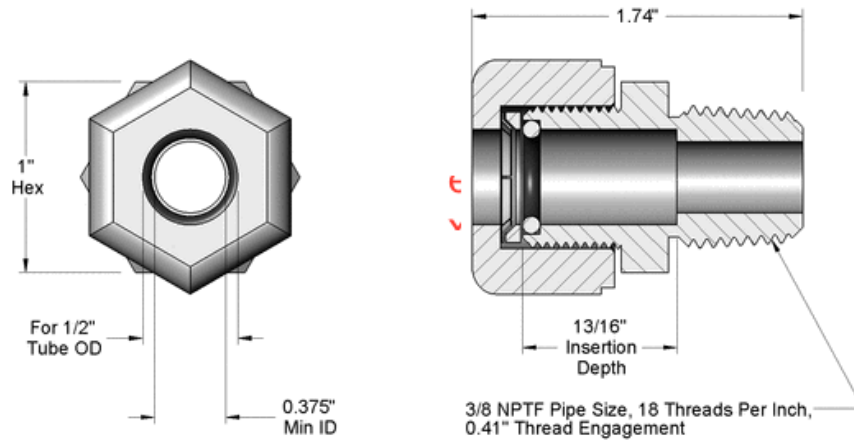
Figure 3-4 Compression fitting

Figure 3-5 Compression fitting and through-wall fitting coupled

The second port is a quick-disconnect tube coupling (McMaster-Carr 5012K98 and 5012K83), which was installed for inlet gas. The inlet port was mainly used for purging the reactors. Figure 3-6 shows the quick-disconnect tube coupling fitting.
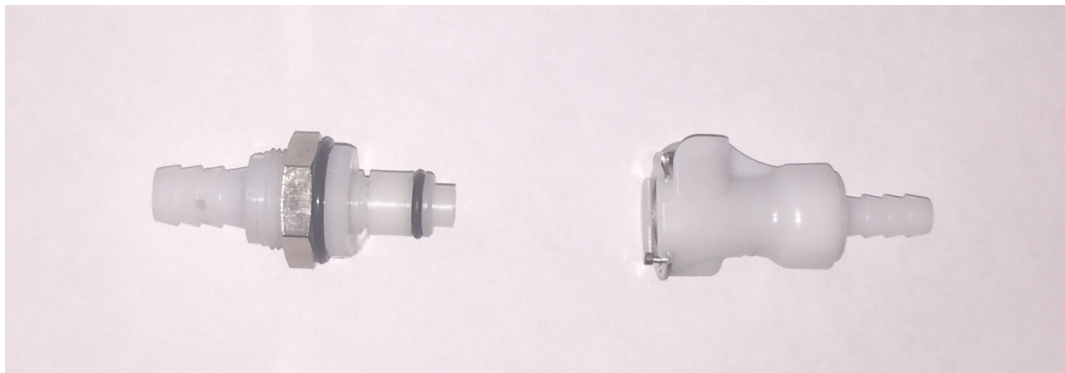
Figure 3-6 Quick-disconnect tube coupling

3.4 Data Collection Method

In order to determine the kinetics of the reactions, the changes in methane and carbon dioxide concentration in the head space were monitored using SRI Instrument, model 8610 C gas chromatograph (GC). Agilent J&W HayeSep column was used to separate CH_4 and CO_2 (p/n G3591-81020). The GC was equipped with a flame ionization detector and utilized helium and hydrogen as carrier and burning gas, respectively. Figure 3-7 shows the GC instrument.
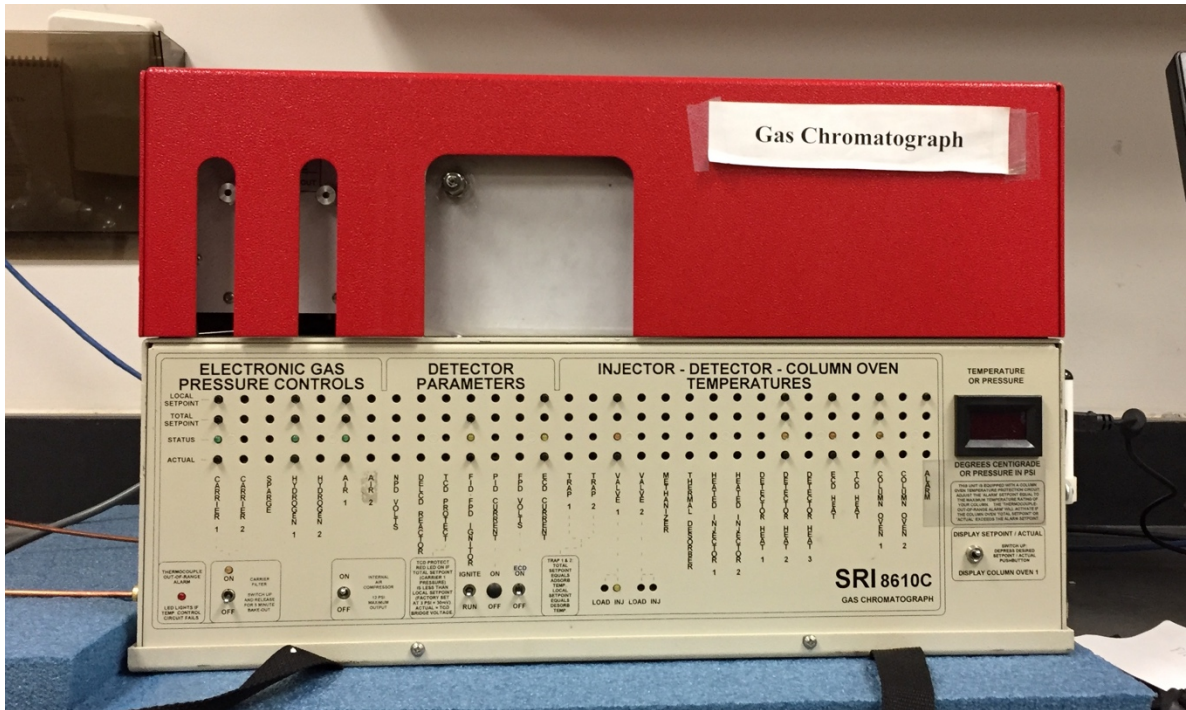
Figure 3-7 SRI Model 8610C Gas Chromatograph

For each data point, a 50 μl sample of head-space gas was collected from the reactor using a sampling syringe, and immediately injected into the GC. Figure 3-8 shows the 100 μl syringe used for sampling.

Figure 3-8 0.1 ml Sampling Syringe

After purging the reactors, the first sample was taken at t=0. The concentration of methane and carbon dioxide were monitored and recorded every 24 hours for 35 days.

The pH of each sample was measured before and after the incubation to evaluate the effect of adding fly ash and incubation on the pH of the mixtures. To measure pH of the solid samples, 3 ml of distilled water was added to 5 g of each sample to produce a slurry. At the end, a probe was used to measure the pH values of slurry samples. The results and findings are discussed in the next chapter.

Chapter 4

Results and Discussion

This chapter includes the results of preliminary tests and batch reactor experiments. The results are presented and discussed to evaluate the effect of fly ash on mitigating CH_4 emissions.

4.1 Preliminary Test Results

Table 4-1 show the results from ESCA. The samples with high Iron and sulfur content are highlighted on the table because of their potential to facilitate oxidation of methane in anaerobic processes. F1, F3 and C1 have the highest iron and sulfur contents. The carbon content of the samples is generally around 5%. As a rule of thumb, the carbon content of 5% or less in the fly ash indicates high efficiency combustion for power plants (Dindarloo et al., 2015). However, F3 sample has 20% carbon content, which means the power plant from which F3 sample came was not operating at optimum conditions.

Table 4-1 ESCA results

Elements	Samples						
	F1	F2	F3	C1	C2	S1	S2
O	63.5	59.5	56.0	61.0	62.3	67.5	65.2
C	5.7	3.8	20.0	6.4	6.0	3.0	3.7
Na	5.5	1.1	1.0	1.3	2.0	0.6	0.7
Ca	0.9	4.5	0.7	4.7	5.1	0.4	0.6
S	7.1	4.0	5.4	4.3	1.4	ND	ND
Si	9.6	12.8	9.6	11.7	12.3	16.1	16.3
Al	3.9	5.5	4.3	6.2	6.2	10.0	11.2
Mg	ND	6.4	ND	3.5	3.2	1.1	1.2
Fe	1.4	0.6	1.3	0.9	0.6	0.9	0.9
K	1.7	0.8	ND	ND	ND	0.4	0.3
N	0.7	ND	1.6	ND	ND	ND	ND
F	ND	0.8	ND	ND	0.7	ND	ND
other	0	0.2	0.1	0	0.2	0	0

The data from ESCA also show nitrogen in the samples present as an organic (e.g. amine or amide) and sulfur is present as sulfate. Silicon is most likely oxides and fluorine is present as fluoride. The data also show aluminum most likely present as Al_2O_3, cobalt as CoO, iron as Fe_2O_3, Mg as MgO, and silicon as SiO_2.

The other factor which was considered to facilitate the process is adsorption capacity of the samples. Figures 4-1 and 4-2 show the results from BET analysis for methane and carbon dioxide, respectively.
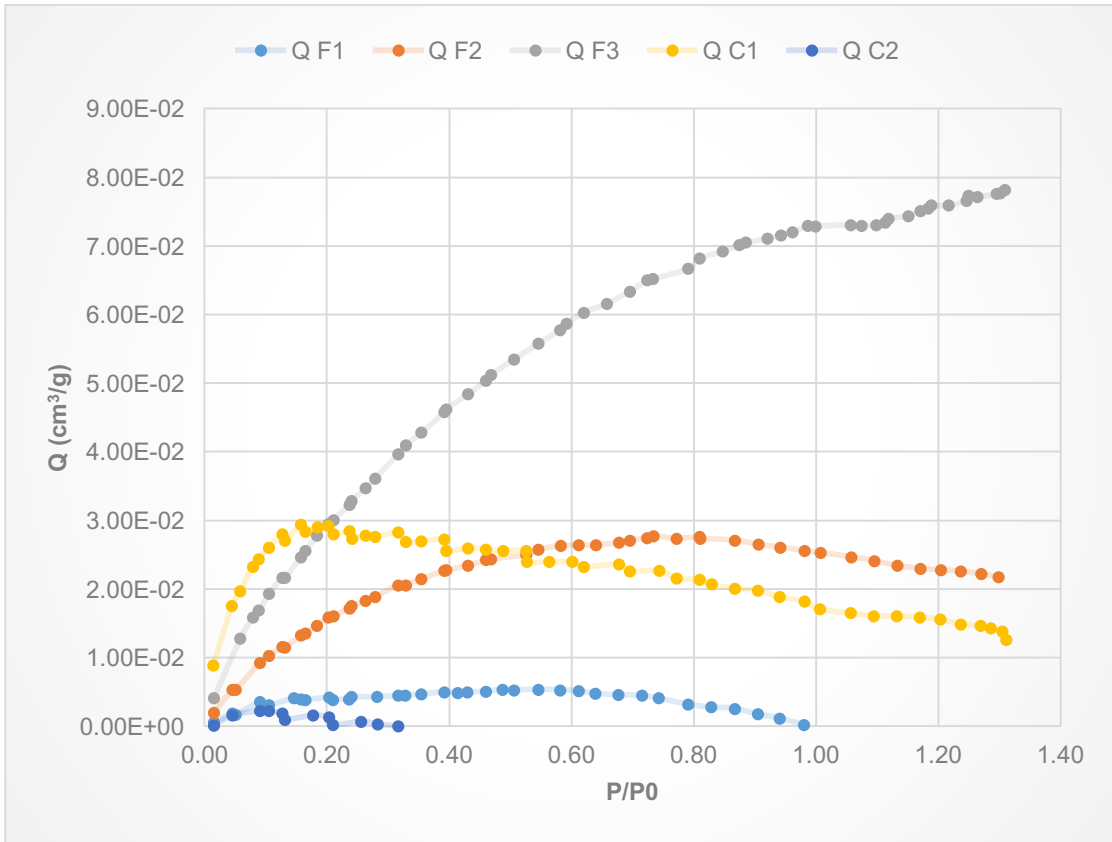
Figure 4-1 Quantity of methane adsorbed vs. relative pressure
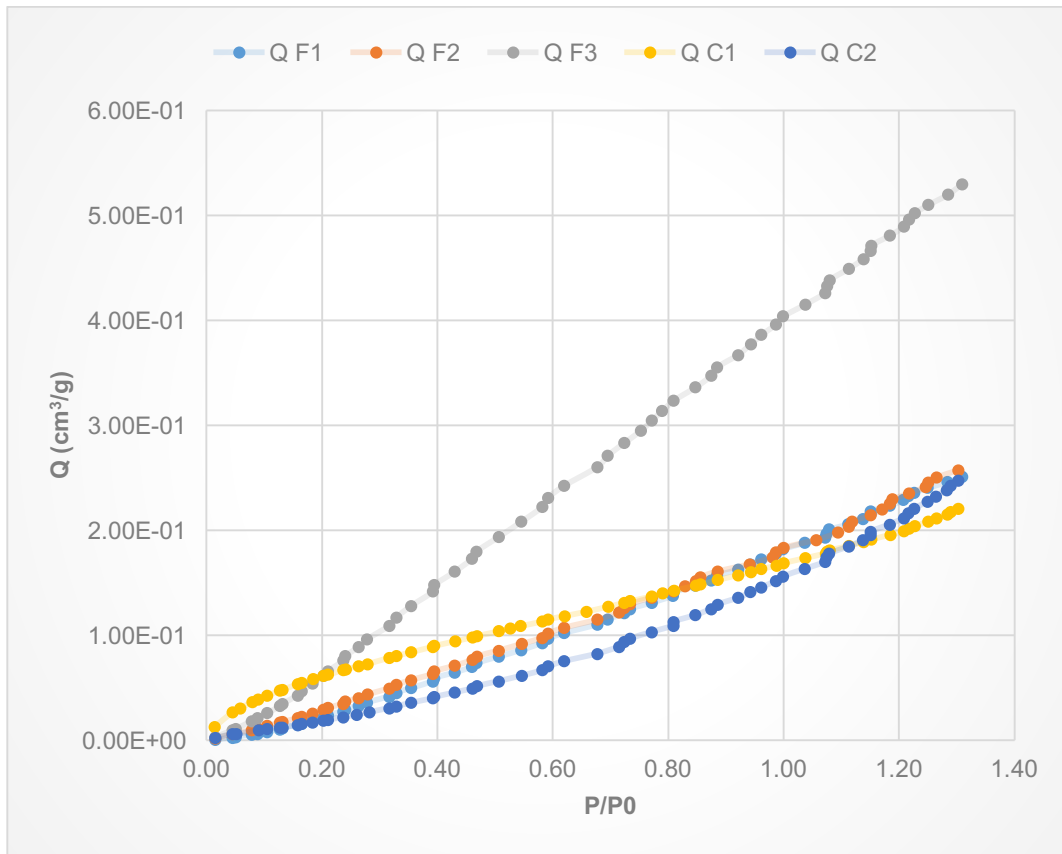
Figure 4-2 Quantity of carbon dioxide adsorbed vs. relative pressure

The BET results show that F3 has the best performance compared to other samples to adsorb CO_2 and CH_4, and it is followed by sample C1 for low values of partial pressure, and sample F2 for high values of partial pressure. The effectiveness of C1 and F2 compared to the other samples is greater for methane than for carbon dioxide. The high carbon content of F3 could be the reason for its higher surface area.

The BET test also reports the partial pressure at which, a single layer adsorption had occurred during the test, which is used to determine the surface area of the samples. Table 4-2 shows the single point surface area result for the fly ash samples.

Table 4-2 BET results for single point surface area

Sample	Surface area (cm^2/g)	
	Methane	Carbon dioxide
F1	0.014	0.118
F2	0.0632	0.1434
F3	0.1191	0.3173
C1	0.0908	0.2389
C2	0.0049	0.0875

Again, the results indicate that F3 and C1 have the highest surface area available for adsorption, for both methane and carbon dioxide.

To choose which fly ash samples to be used in our experiment, the selection criteria were as follows:

- The selected fly ashes should include both types of fly ash (F and C),
- High surface area is desirable (high adsorption capacity for CH_4),
- High concentration of sulfur and Iron are preferred.

The fly ash samples F3 and C1 were chosen for the experiment since they met all the criteria above. The sulfur and iron content in all F type fly ashes were relatively high. However, the adsorption capacity of F1 and F2 were significantly lower than F3 for both CH_4 and CO_2. C1 was chosen over C2 because C1 had higher adsorption capacity and higher iron and sulfur content.

4.2 Batch Reactor Experiment Results:

In order to evaluate the performance of soil-fly ash mixture to mitigate methane, the kinetic of methane oxidation should be determined for each sample. There are two major factors affecting the change in methane concentration. Besides methane oxidation (the factor we are looking at), a fair amount of methane is being adsorbed during the experiment. To find the true rate of oxidation, the adsorption kinetics should be deducted from the experiment results.

In addition to methane concentration, the CO_2 concentration was measured and recorded. CO_2 is a product of methane oxidation. As methane oxidation happens, the amount of CO_2 in the reactor should increase. In the case where adsorption kinetics are dominant, the CO_2 concentration should decline. Tracking the CO_2 concentration could help validating the methane oxidation, especially in case of a leakage in the system.

Figures 4-3 to 4-14 show the plotted results for all 6 reactors Assuming a first-order process (which could either be adsorption or microbial oxidation or a combination):

$C = C_o \exp(-kt)$

$\ln(C/C_o) = -kt$

Since the plots show $\ln(C/C_o)$ vs. t, the slope gives the first-order rate-constant k. Using a thin layer of sample in the experiment eliminated mass transfer limitations; therefore, adsorption follows first-order kinetics similar to methane oxidation.

Each figure shows two phases of experiment, differentiated by a change in slope. Lag phase, marked with blue color, is hypothesized to show the concentration of CH_4 and CO_2 in the absence of microbial activity. The decline in methane concentration in the Lag

phase is presumably caused by physical adsorption. The lack of food (methane) and aerobic environment prior to incubation caused methanogens to hibernate in order to survive. The Lag phase was estimated to be 12 days using trial and error.

Active phase, marked with red color, is hypothesized for reactors 2, 5, and 6 to show CH_4 and CO_2 concentration changes due to adsorption and microbial activity. The increased slope could also have represented a second adsorption layer (gas-to-gas instead of gas-to-solid). An increase in methane uptake rate during the Active phase for these 3 reactors is indicated by an increased slope of the graph. Thus the methane oxidation rate coefficient could be estimated by subtracting the results of two phases.

For reactors 1 and 3, containing Soil 1, the methane slope decreases from Lag phase to Active phase. For reactor 4, the methane slope increases, but so does the CO_2 slope. Apparent lack of microbial activity could have been due to lack of available moisture. Purging of the reactors prior to the experiments could have reduced the moisture level below what the microbes require.
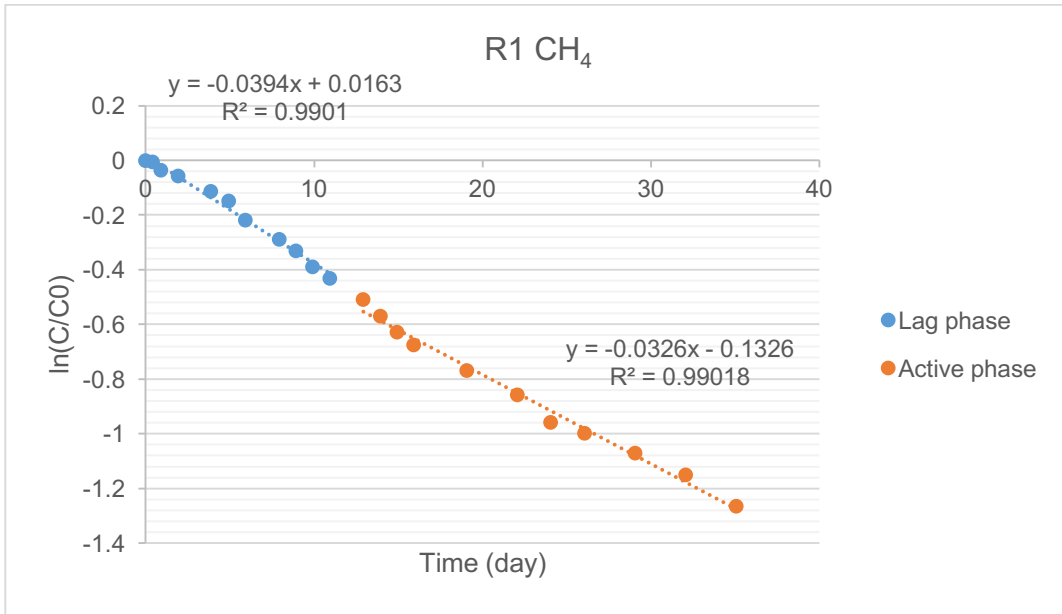
Figure 4-3 Dimensionless conc. of CH_4 vs. time for R1 (100% Soil 1)
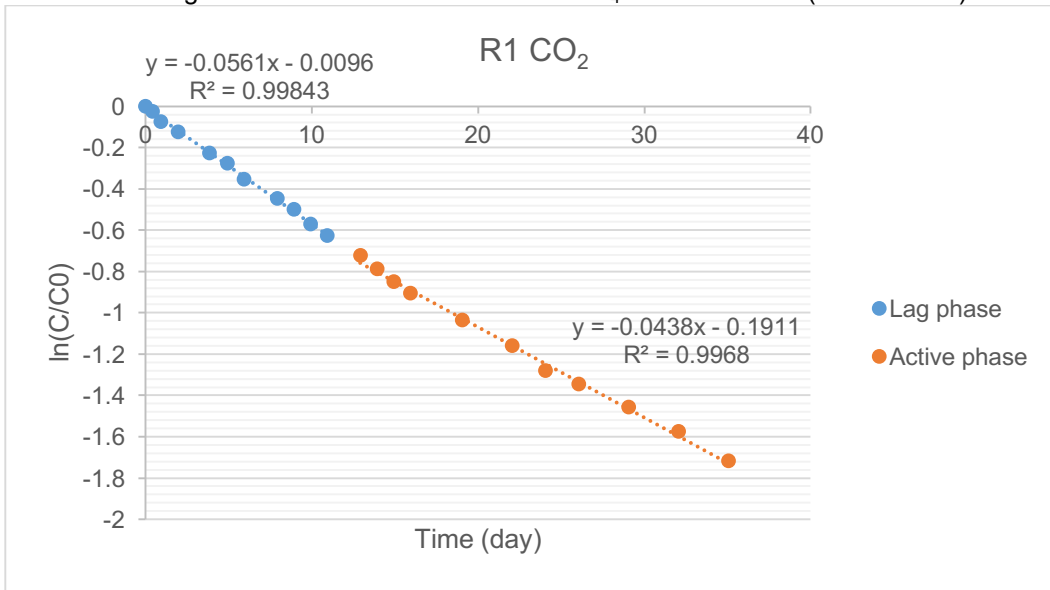
Figure 4-4 Dimensionless conc. of CO_2 vs. time for R1 (100% Soil 1)
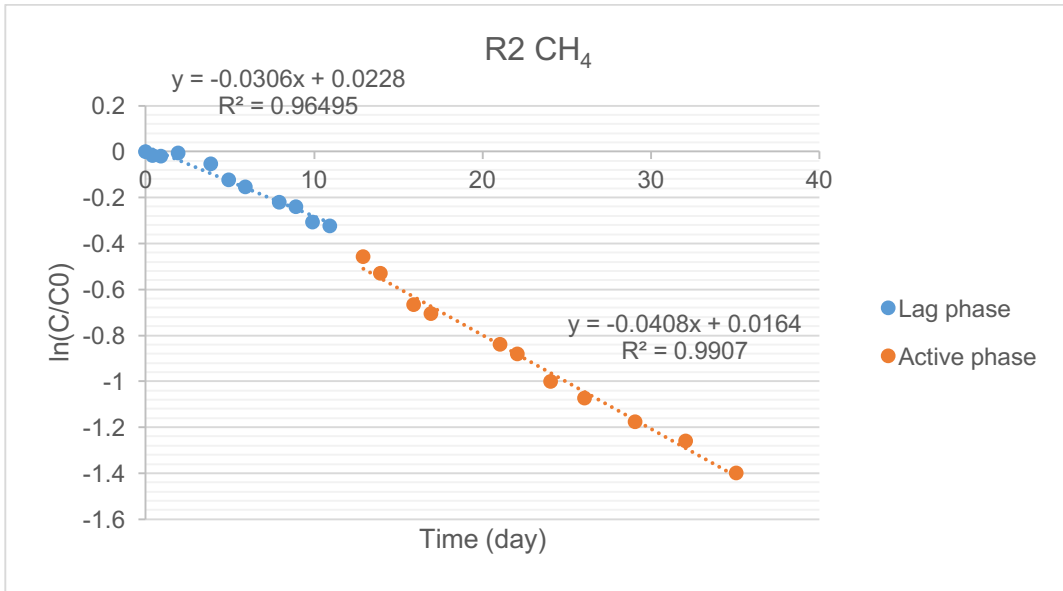
Figure 4-5 Dimensionless conc. of CH_4 vs. time for R2 (100% Soil 2)
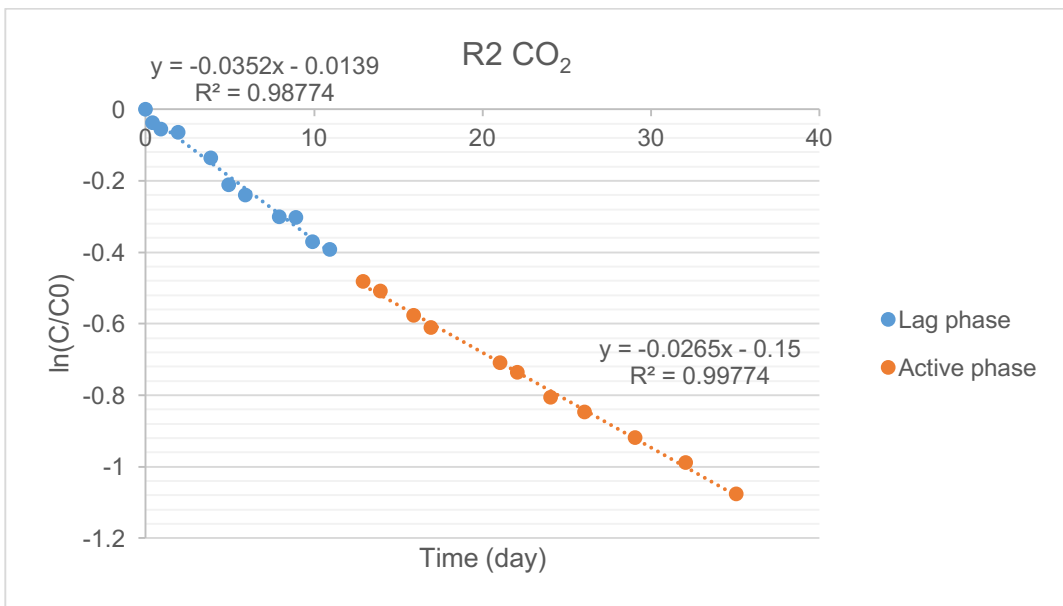
Figure 4-6 Dimensionless conc. of CO_2 vs. time for R2 (100% Soil 2)

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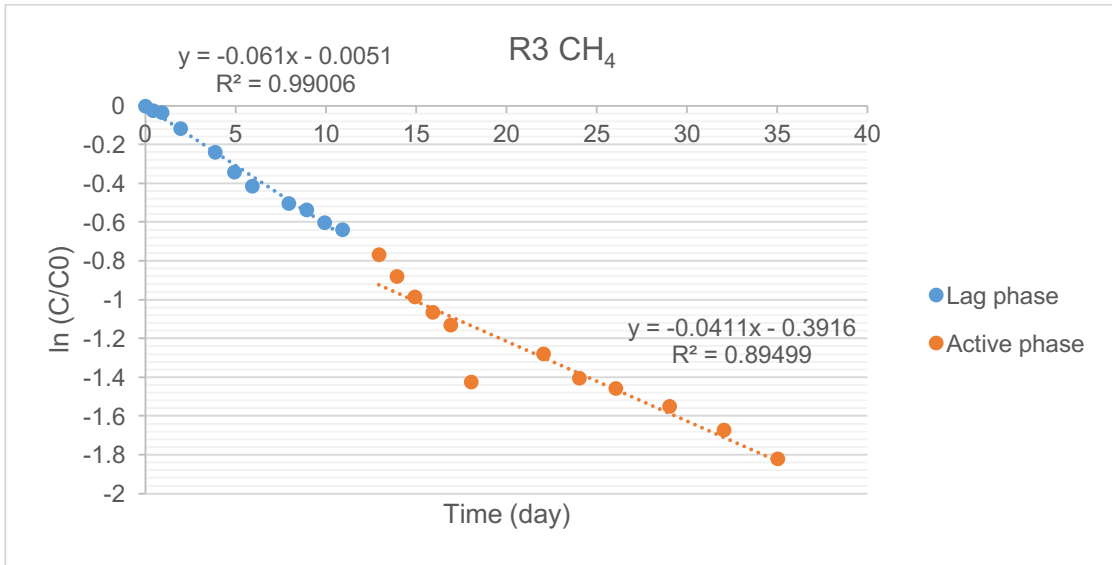
Figure 4-7 Dimensionless conc. of CH_4 vs. time for R3 (75% Soil 1, 25% fly ash C1)
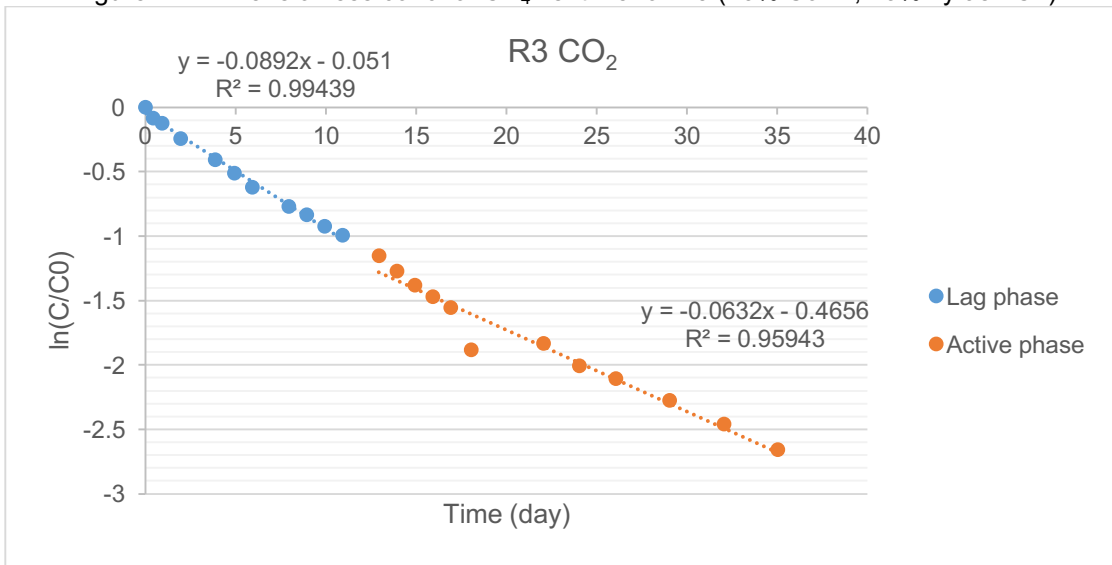
Figure 4-8 Dimensionless conc. of CO_2 vs. time for R3 (75% Soil 1, 25% fly ash C1)
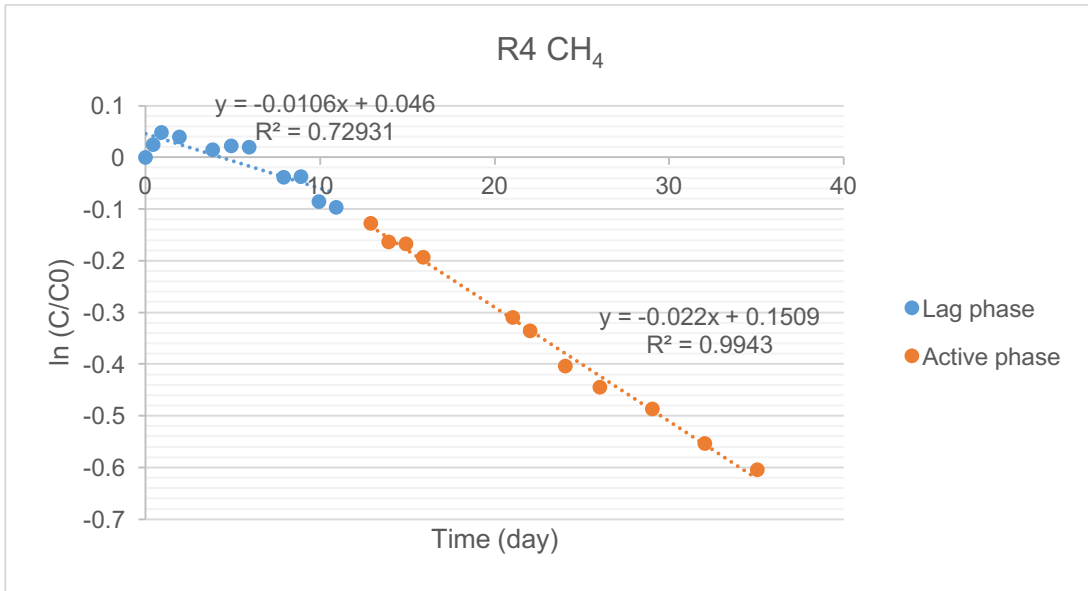
Figure 4-9 Dimensionless conc. of CH_4 vs. time for R4 (75% Soil 2, 25% fly ash C1)
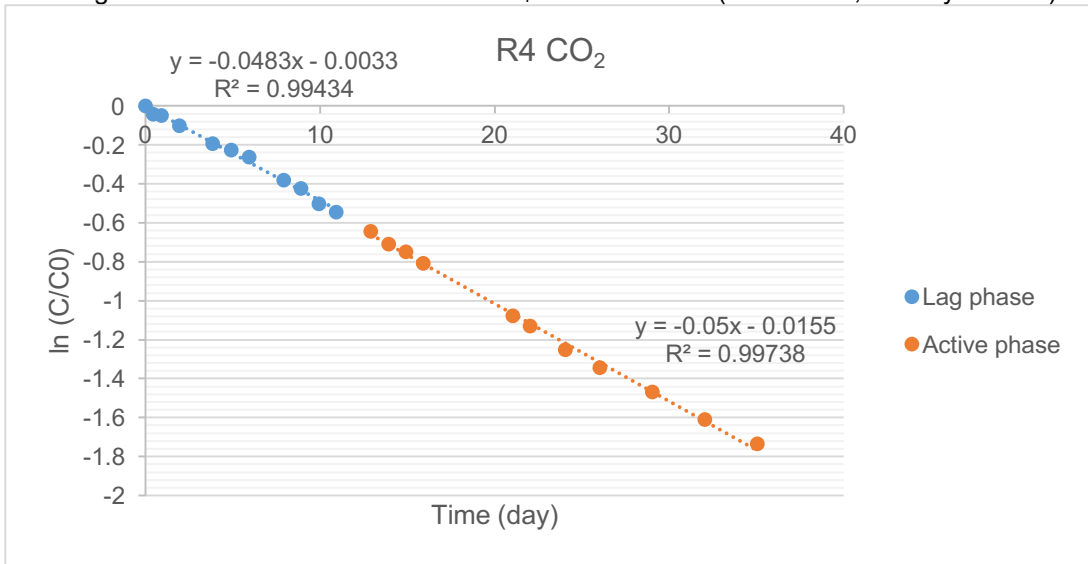
Figure 4-10 Dimensionless conc. of CO_2 vs. time for R4 (75% Soil 2, 25% fly ash C1)
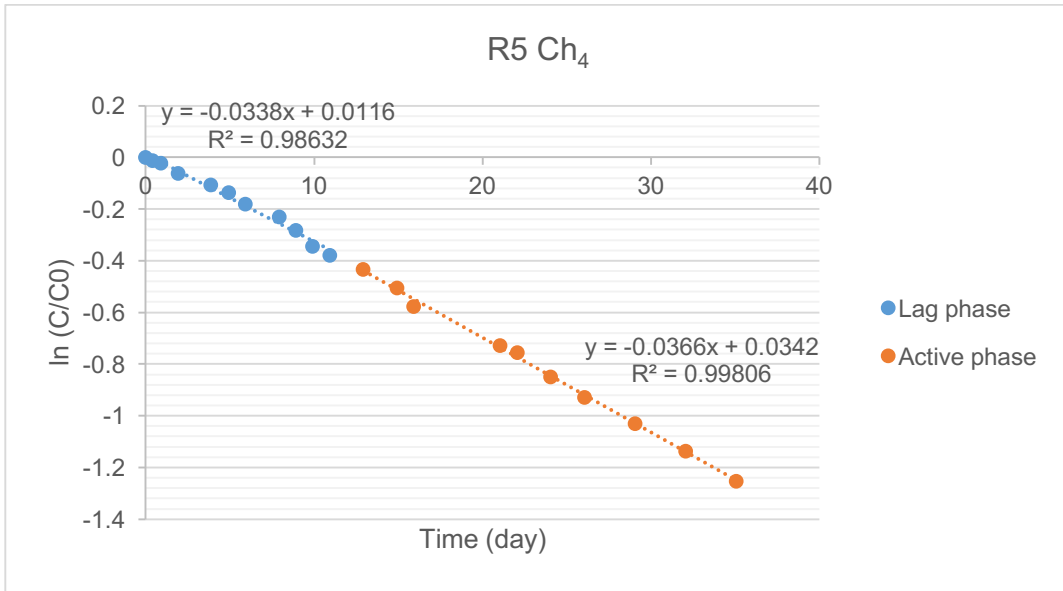
Figure 4-11 Dimensionless conc. of CH_4 vs. time for R5 (75% Soil 1, 25% fly ash F3)
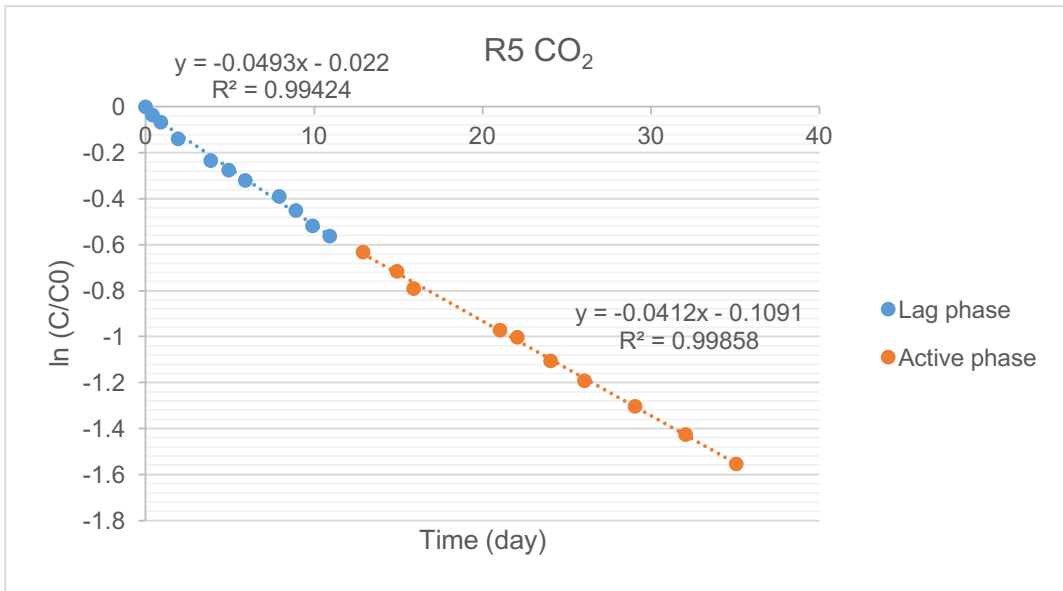
Figure 4-12 Dimensionless conc. of CO_2 vs. time for R5 (75% Soil 1, 25% fly ash F3)
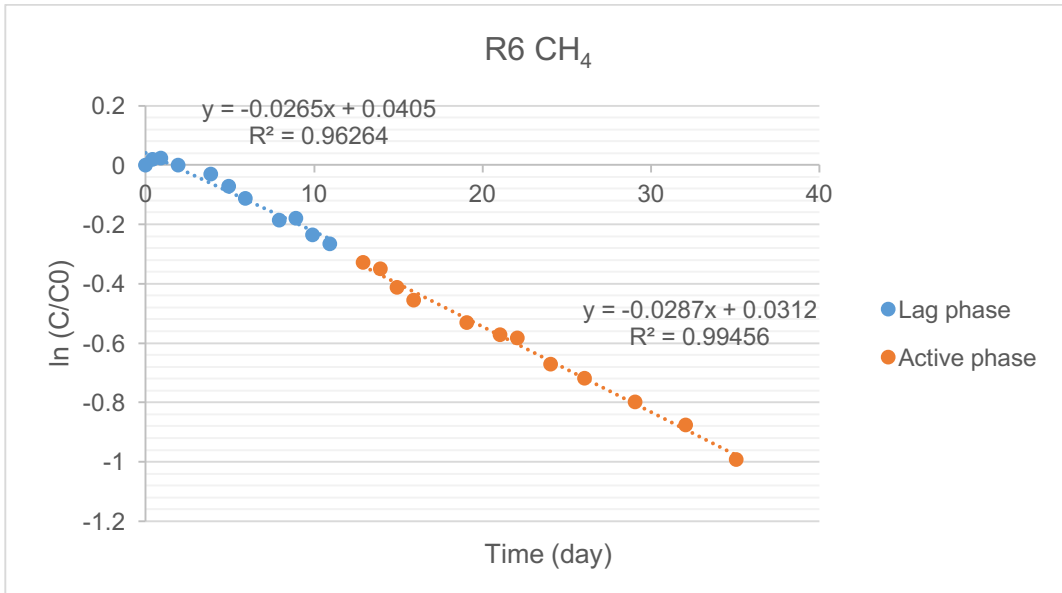
Figure 4-13 Dimensionless conc. of CH_4 vs. time for R6 (75% Soil 2, 25% fly ash F3)
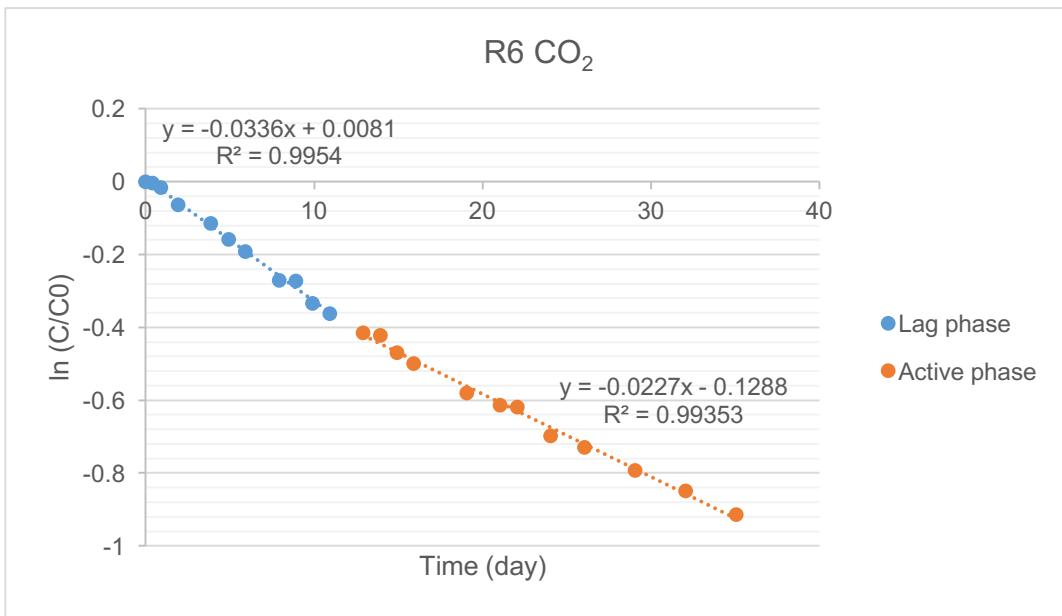
Figure 4-14 Dimensionless conc. of CO_2 vs. time for R6 (75% Soil 2, 25% fly ash F3)

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Table 4-3 summarizes the k rate constant values obtained from the results. A change that is positive for methane and negative for CO_2, and approximately equal in magnitude, would indicate conversion of methane into CO_2. This is the case for R2.

Table 4-3 Summary of k values

Reactor	CH$_4$		Change	CO$_2$		Change
	Lag phase	Active phase		Lag phase	Active phase	
R1 (100% soil S1)	0.0394	0.0326	-0.0231	0.0561	0.0438	-0.0123
R2 (100% soil S2)	0.0306	0.0408	0.0102	0.0352	0.0265	-0.0087
R3 (75% soil S1, 25% fly ash C1)	0.061	0.0411	-0.0199	0.0892	0.0632	-0.026
R4 (75% soil S2, 25% fly ash C1)	0.0106	0.022	0.0114	0.0483	0.05	0.0017
R5 (75% soil S1, 25% fly ash F3)	0.0338	0.0366	0.0028	0.0493	0.0412	-0.0081
R6 (75% soil S2, 25% fly ash F3)	0.0265	0.0287	0.0022	0.0336	0.0227	-0.0109

To discuss the results in detail, the samples were separated by the type of soil.

- R1, R3 and R5 containing S1 soil:

The graphs from the reactors containing the S1 soil sample have high R^2 values for both CH$_4$ and CO_2, with a slight change in slope from Lag phase to Active phase. For reactors 1 and 3, the methane slope decreases from Lag phase to Active phase. For reactor 5, it increases. For all 3 reactors, the CO_2 slope decreased from Lag phase to Active phase.

Also, the highest adsorption rates for methane and CO_2 were measured for R3. The CO_2 slope in the Active phase decreased. The adsorption would reach its equilibrium faster if the rate of adsorption is higher. The decrease in CO_2 slopes for

R3 could possibly have been caused by a second layer of adsorption of CO_2 occurring, with less attraction between CO_2 molecules compared with the CO_2-solid attraction for the first layer.

The adsorption rates in R5 was measured to be less than R1 and R3. Also k value changes between two phases are less significant, compared to other (R1 and R3) reactors. Despite the facts that BET results indicates higher adsorption for F3, the adsorption kinetic of R5 is slower than the other reactors. Lesser deviations of k value from Lag phase to Active phase also suggests that R5 went through a longer period of single-layer adsorption.

- R2, R4 and R6 containing S2 soil:

For the reactors containing the S2 soil sample, the slopes of the methane graphs increase from Lag phase to Active phase, indicating potential methane removal due to microbial activity. The slope of CO_2 concentration decreases in the case of R2 and R6, indicating that CO_2 may be biologically produced by conversion of methane during the Active phase. Even though adsorption of CO_2 is still occurring, the overall rate of loss of CO_2 from the reactor headspace may be slowed due to conversion of methane to CO_2 during Active phase. For reactor 4, however, the CO_2 slope increases slightly from the Lag phase to Active phase.

For reactor 4, the increase in methane concentration at the beginning of the experiment may indicate the fact that in addition to methantrophs, the S2 soil sample also contains methanogen microbes. The methanogens in the sample are active and since the experiment is done in an anaerobic environment, methanogens can obtain CO_2 or other

hydrocarbons as electron donor and convert them to CH_4. The potential activity of methanogens adds many unknowns to the system. There are many factors which have not been monitored and can affect the activity of the microbes, such as electron donor source (and its limitation), pH of the system, temperature and many others that would change the kinetics of the reaction.

The batch reactor data was analyzed in a second way. Microbial methane oxidation will reduce the concentration of methane and increase the concentration of carbon dioxide. Using molar concentration ratio of CO_2 and CH_4 through the experiment would be a good indicator to evaluate the performance of samples. This ratio would be affected by adsorption kinetics, but if the ratio exceeds 1 (considering the fact that initial concentrations were close), it indicates a high rate of oxidation, considering the fact that CO_2 is highly favored over CH_4 to be adsorbed in all the samples. Figure 4-15 and 4-16 show the molar concentration ratio of CO_2 and CH_4 versus time for reactors containing S1 and S2, respectively.
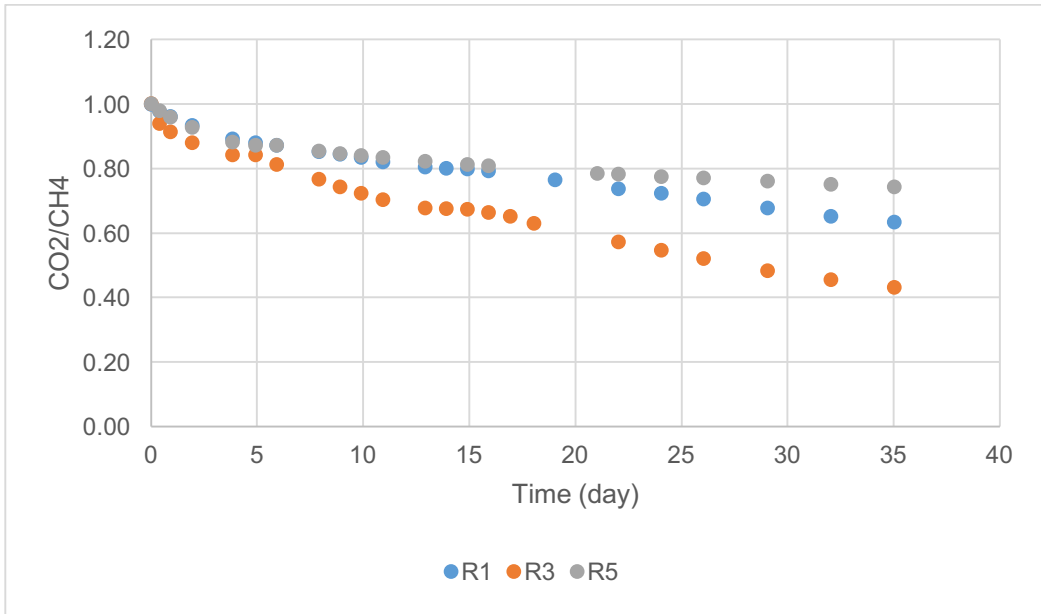
Figure 4-15 Molar conc. ratio of CO_2 and CH_4 for reactors containing soil S1
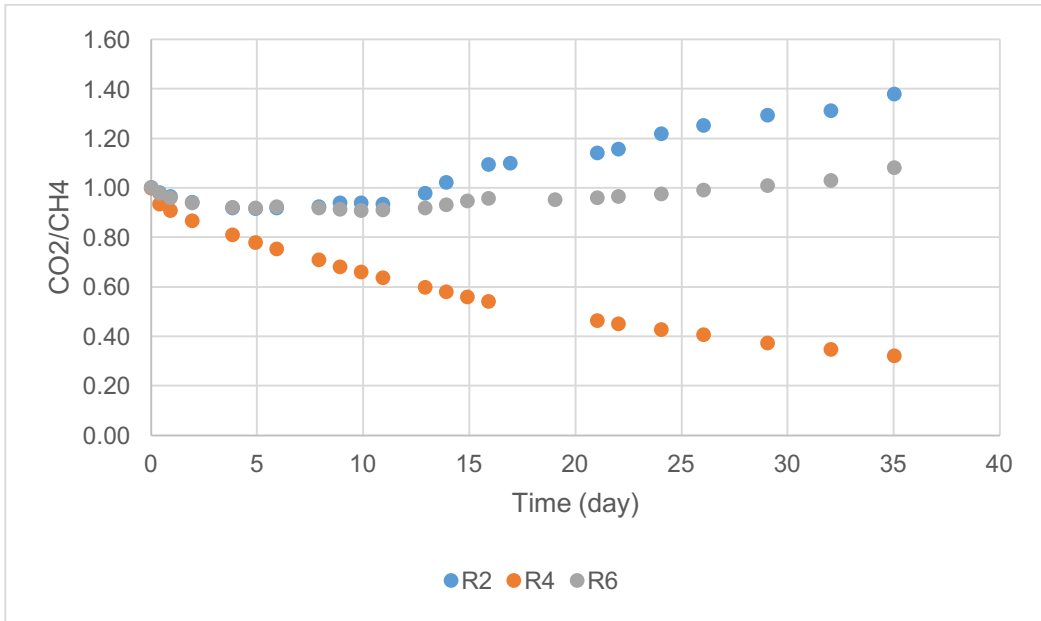
Figure 4-16 Molar conc. ratio of CO_2 and CH_4 for reactors containing soil S2

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From Figure 4-15, it can be inferred that adsorption is the dominant process occurring in the reactors. There is a uniform and steady decline in CO_2/CH_4 over time for all the reactors. The decline is due to the fact that the CO_2 adsorption rate is higher than CH_4 adsorption. The steady decline of CO_2/CH_4 without any significant change indicates the fact that there is no microbial activity throughout the process. The decrease in CO_2/CH_4 shows the preference of sample to adsorb CO_2.

Figure 4-16 shows a similar trend for reactor 4, but a different trend for reactors 2 and 6. For reactors 2 and 6, 6he trend changes after 10 days of incubation and the CO_2/CH_4 begins to increase. The highest CO_2/CH_4 is reached by R2, showing the best performance was achieved by soil sample by itself. The 2 reactors containing fly ash (R4 and R6) did not perform as well in terms of microbial oxidation.

High amount of fly ash in samples can cause a decrease in microbial activity. Many of the observed chemical and biological effects of fly ash applications to soils resulted from the increased activities of Ca^{2+} and OH^- ions which can increase the pH, which would inhibit the activity of methanotrophs (Adriano et al, 1979). Excessive use of fly ash also can increase the salinity of soil and inhibit the microbial activity. To address this issue, the pH of samples was measured by increasing the moisture content of samples to 60%. Results from slurry samples are rough estimates of the sample's pH under experimental conditions. Table 4-4 shows the pH of samples at the end of the experiment and fly ash samples by themselves.

Table 4-4 pH results at the end of the experiment

Sample	pH after incubation	pH w/o incubation
C1	12.66	-
F3	4.09	-
R1 (S1)	6.49	6.41
R2 (S2)	6.75	6.63
R3 (S1 + C1)	8.15	8.12
R4 (S2 + C1)	8.17	8.11
R5 (S1 +F3)	6.75	6.19
R6 (S2 + F3)	6.81	6.27

From the results, class C fly ash has alkalinity potential in aqueous environment. As was mentioned earlier, class C fly ashes are associated with high concentration of $CaCO_3$, which is a source of alkalinity. On the other hand, class F fly ash has limited amount of $CaCO_3$. In case of F3, high carbon content would be the source of acidity. The high sulfate (SO_4^{2-}) content of samples would not contribute to the alkalinity since sulfuric acid has high K_a values. The pH of soils are in the typical range for clay soil, which is 5.5 to 7 (Anderson et. al, 1988).

The pH results for R5 and R6 shows an increase in soil and fly ash mixtures after incubation, while the pH was expected to be less than the results for soil samples. The release of CO_2 adsorbed on F3 fly ash would be one the explanations. Also, some of methane oxidation processes, as it was mentioned in Chapter 2, would uptake protons in their process. The buffering nature of soils, however, would resist high pH changes.

The concentrations of elements in the fly ash with the potential to oxidize methane (e.g. iron, manganese) were low for the fly ashes tested; in addition, the large fraction of fly ash used (25%) substantially reduced the microbes available for methane oxidation. The optimum pH for methanothrophic activity is close to neutral (Tajul Islam et. al, 2014). High alkalinity of C1 increased the pH of samples over 8, which would limit microbial growth and activity. This result could explain the low oxidation of methane in R4. Fly ash or other wastes with a higher percent of constituents like iron and manganese could be tested, in lower fractions.

Chapter 5

Conclusions and Recommendations

The main objective of this research was to evaluate the effect of using fly ash as an additive to landfills final cover, in order to enhance the anaerobic methane oxidation.

The greatest potential methane oxidation was achieved in a sample of soil by itself. Reactor R2 containing soil S2 alone had the second highest change in k value from Lag phase to Active phase. Also, the highest ratio of CO_2/CH_4 (approximately 1.4) at the end of the experiment, indicates the fact that microbes had converted CH_4 to CO_2. R6 reactor containing 75% S2 soil sample and 25% F3 fly ash had the second best performance with a CO_2/CH_4 ratio of 1.1 at the end of the experiment. Addition of C1 fly ash to S2 soil sample caused an increase in pH of the sample and inhibited the microbial activity in R4.

Results from reactors containing S2 soil sample indicate the fact that S2 contained insufficient number of microbes to perform methane oxidation. The steady and continuous decline of gas concentrations in R1, R3 and R5 showed the insignificance of microbial activity. The incline in K values from Lag Phase to Active Phase in the reactors, and also low values of CO_2/CH_4 ratio at the end of 35-day period proves the dominance of adsorption for these reactors.

The addition of fly ash did not enhance methane oxidation. However, the concentrations of elements in the fly ash with the potential to oxidize methane (e.g. iron, manganese) were low in the fly ashes tested; in addition, the large fraction of fly ash used (25%) substantially reduced the microbes available for methane oxidation. Fly ash or

other wastes with a higher percent of constituents like iron and manganese should be tested, in lower fractions.

The other reason which affected the performance of samples containing fly ash was the amount of soil. The amount of microbes in the mixture is proportional to the amount of soil in the samples. In this study, comparison was made between the final amount of samples. The reason for this is that increasing the amount of final cover is not practical. Using higher volume of material for final cover would not increase the final covers effectiveness. Lower portion of soil wouldn't be compacted. Adding fly ash to the same amount of soil for final cover would decrease the available space for solid waste deposition.

Since methane oxidation enhancement was prior to fly ash deposition, it is not reasonable for it to be used as an amendment. Fly ash with high amount of metal oxides is potentially a source of contamination for ambient surface water and air.

Based on the results and experiences from this project, the following recommendations are made for future study:

- Test samples with less than 20% of fly ash to avoid high salinity and raising pH.
- Dilute methane with an inert gas instead of purging the reactors to save time and avoiding errors from permeation.
- Test other sources waste sources which have a higher iron content than fly ash.
- Add controls of fly ashes by themselves, as well as an empty reactor by itself.
- Purge the reactors with an inert gas to avoid adding any methane to the sample during purging, and to remove any previously adsorbed methane.
- Check the methane and oxygen that is exiting the system during purging. When

the values go to zero, the system is ready for experiments.

- Run an experiment with soil in nitrogen reach environment, to determine whether any methane generation occurs.

- Obtain multiple XPS readings from each sample, to determine whether the differences in percent composition of the various fly ashes are statistically significant.

- Identify the microorganisms in the soil, before and after experiment.

- Measure moisture content before and after purging. If purging affects on moisture content are significant, more water should be added to the samples before starting the experiment.

Appendix A

Batch Reactor Results

Results for R1 reactor containing S1

Time (day)	GC Area		Molar Conc.		ln(C/Co)	
	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
0.0	8135	8141	3.05E-02	3.33E-02	0.000	0.000
0.4	8100	7926	3.04E-02	3.24E-02	-0.004	-0.027
0.9	7857	7558	2.95E-02	3.09E-02	-0.035	-0.074
1.9	7684	7177	2.88E-02	2.94E-02	-0.057	-0.126
3.9	7266	6494	2.72E-02	2.66E-02	-0.113	-0.226
4.9	7014	6178	2.63E-02	2.53E-02	-0.148	-0.276
5.9	6542	5717	2.45E-02	2.34E-02	-0.218	-0.353
7.9	6102	5203	2.29E-02	2.13E-02	-0.288	-0.448
8.9	5851	4941	2.19E-02	2.02E-02	-0.330	-0.499
9.9	5512	4605	2.07E-02	1.88E-02	-0.389	-0.570
10.9	5293	4351	1.98E-02	1.78E-02	-0.430	-0.627
12.9	4896	3946	1.84E-02	1.61E-02	-0.508	-0.724
13.9	4611	3699	1.73E-02	1.51E-02	-0.568	-0.789
14.9	4343	3477	1.63E-02	1.42E-02	-0.628	-0.851
15.9	4151	3294	1.56E-02	1.35E-02	-0.673	-0.905
16.9	3083	2439	1.42E-02	1.18E-02	-0.970	-1.205
21.0	2031	1504	1.30E-02	1.04E-02	-1.388	-1.689
24.0	3123	2261	1.17E-02	9.25E-03	-0.957	-1.281
26.0	3004	2121	1.13E-02	8.68E-03	-0.996	-1.345
29.0	2792	1895	1.05E-02	7.75E-03	-1.070	-1.458
32.0	2580	1684	9.67E-03	6.89E-03	-1.149	-1.575
35.0	2298	1459	8.62E-03	5.97E-03	-1.264	-1.719

Results for R2 reactor containing S2

Time (day)	GC Area		Molar Conc.		ln(C/Co)	
	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
0.0	8091	8112	3.03E-02	3.32E-02	0.000	0.000
0.4	7962	7812	2.99E-02	3.20E-02	-0.016	-0.038
0.9	7938	7671	2.98E-02	3.14E-02	-0.019	-0.056
1.9	8048	7602	3.02E-02	3.11E-02	-0.005	-0.065
3.9	7689	7081	2.88E-02	2.90E-02	-0.051	-0.136
4.9	7165	6574	2.69E-02	2.69E-02	-0.122	-0.210
5.9	6952	6388	2.61E-02	2.61E-02	-0.152	-0.239
7.9	6499	6011	2.44E-02	2.46E-02	-0.219	-0.300
8.9	6377	5991	2.39E-02	2.45E-02	-0.238	-0.303
9.9	5956	5601	2.23E-02	2.29E-02	-0.306	-0.370
10.9	5858	5479	2.20E-02	2.24E-02	-0.323	-0.392
12.9	5123	5015	1.92E-02	2.05E-02	-0.457	-0.481
13.9	4765	4881	1.79E-02	2.00E-02	-0.529	-0.508
14.9	5212	5595	1.56E-02	1.86E-02	-0.440	-0.371
16.9	4001	4408	1.50E-02	1.80E-02	-0.704	-0.610
18.0	1759	1925	1.31E-02	1.63E-02	-1.526	-1.439
22.0	3355	3885	1.26E-02	1.59E-02	-0.880	-0.736
24.0	2975	3627	1.12E-02	1.48E-02	-1.000	-0.805
26.0	2774	3481	1.04E-02	1.42E-02	-1.070	-0.846
29.0	2499	3237	9.37E-03	1.32E-02	-1.175	-0.919
32.0	2299	3018	8.62E-03	1.23E-02	-1.258	-0.989
35.0	2001	2765	7.51E-03	1.13E-02	-1.397	-1.076

Results for R3 reactor containing 75% S1 and 25% F3

Time	GC Area		Molar Conc.		ln(C/Co)	
(day)	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
0.0	8057	8070	3.02E-02	3.30E-02	0.000	0.000
0.4	7872	7403	2.95E-02	3.03E-02	-0.023	-0.086
0.9	7791	7119	2.92E-02	2.91E-02	-0.034	-0.125
1.9	7169	6321	2.69E-02	2.59E-02	-0.117	-0.244
3.9	6338	5349	2.38E-02	2.19E-02	-0.240	-0.411
4.9	5726	4830	2.15E-02	1.98E-02	-0.342	-0.513
5.9	5329	4337	2.00E-02	1.77E-02	-0.413	-0.621
7.9	4871	3738	1.83E-02	1.53E-02	-0.503	-0.770
8.9	4712	3505	1.77E-02	1.43E-02	-0.537	-0.834
9.9	4414	3193	1.66E-02	1.31E-02	-0.602	-0.927
10.9	4249	2989	1.59E-02	1.22E-02	-0.640	-0.993
12.9	3742	2542	1.40E-02	1.04E-02	-0.767	-1.155
13.9	3345	2262	1.25E-02	9.25E-03	-0.879	-1.272
14.9	3006	2030	1.13E-02	8.30E-03	-0.986	-1.380
15.9	2785	1852	1.04E-02	7.58E-03	-1.062	-1.472
16.9	2603	1701	9.76E-03	6.96E-03	-1.130	-1.557
18.0	1939	1224	7.27E-03	5.01E-03	-1.424	-1.886
24.0	1980	1085	8.42E-03	5.26E-03	-1.404	-2.007
26.0	1877	979	7.42E-03	4.44E-03	-1.457	-2.109
29.0	1714	829	7.04E-03	4.00E-03	-1.548	-2.275
32.0	1513	690	6.43E-03	3.39E-03	-1.672	-2.459
35.0	1305	565	5.67E-03	2.82E-03	-1.821	-2.660

Results for R4 reactor containing 75% S2 and 25% F3

Time (day)	GC Area		Molar Conc.		ln(C/Co)	
	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
0.0	8025	8036	3.01E-02	3.29E-02	0.000	0.000
0.4	8228	7707	3.09E-02	3.15E-02	0.025	-0.042
0.9	8424	7653	3.16E-02	3.13E-02	0.049	-0.049
1.9	8351	7260	3.13E-02	2.97E-02	0.040	-0.102
3.9	8144	6617	3.05E-02	2.71E-02	0.015	-0.194
4.9	8211	6414	3.08E-02	2.62E-02	0.023	-0.226
5.9	8192	6183	3.07E-02	2.53E-02	0.021	-0.262
7.9	7729	5488	2.90E-02	2.24E-02	-0.038	-0.381
8.9	7737	5274	2.90E-02	2.16E-02	-0.037	-0.421
9.9	7375	4873	2.77E-02	1.99E-02	-0.085	-0.500
10.9	7290	4657	2.73E-02	1.90E-02	-0.096	-0.546
12.9	7067	4229	2.65E-02	1.73E-02	-0.127	-0.642
13.9	6821	3955	2.56E-02	1.62E-02	-0.163	-0.709
14.9	6795	3809	2.55E-02	1.56E-02	-0.166	-0.747
15.9	6619	3590	2.48E-02	1.47E-02	-0.193	-0.806
16.9	4712	2501	2.21E-02	1.12E-02	-0.532	-1.167
22.0	5743	2598	2.15E-02	1.06E-02	-0.335	-1.129
24.0	5365	2301	2.01E-02	9.41E-03	-0.403	-1.251
26.0	5150	2096	1.93E-02	8.57E-03	-0.444	-1.344
29.0	4935	1852	1.85E-02	7.57E-03	-0.486	-1.468
32.0	4613	1607	1.73E-02	6.57E-03	-0.554	-1.610
35.0	4388	1418	1.65E-02	5.80E-03	-0.604	-1.735

Time	GC Area		Molar Conc.		ln(C/Co)	
(day)	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
0.0	8117	8140	3.04E-02	3.33E-02	0.000	0.000
0.4	8027	7860	3.01E-02	3.21E-02	-0.011	-0.035
0.9	7941	7622	2.98E-02	3.12E-02	-0.022	-0.066
1.9	7628	7085	2.86E-02	2.90E-02	-0.062	-0.139
3.9	7303	6454	2.74E-02	2.64E-02	-0.106	-0.232
4.9	7090	6189	2.66E-02	2.53E-02	-0.135	-0.274
5.9	6778	5914	2.54E-02	2.42E-02	-0.180	-0.319
7.9	6446	5512	2.42E-02	2.25E-02	-0.230	-0.390
8.9	6128	5189	2.30E-02	2.12E-02	-0.281	-0.450
9.9	5759	4850	2.16E-02	1.98E-02	-0.343	-0.518
10.9	5555	4640	2.08E-02	1.90E-02	-0.379	-0.562
12.9	5260	4330	1.97E-02	1.77E-02	-0.434	-0.631
13.9	4662	3807	1.84E-02	1.63E-02	-0.554	-0.760
15.9	4567	3693	1.71E-02	1.51E-02	-0.575	-0.790
16.9	3309	2676	1.47E-02	1.26E-02	-0.897	-1.113
22.0	3816	2988	1.43E-02	1.22E-02	-0.755	-1.002
24.0	3478	2700	1.30E-02	1.10E-02	-0.847	-1.104
26.0	3207	2474	1.20E-02	1.01E-02	-0.928	-1.191
29.0	2902	2211	1.09E-02	9.04E-03	-1.029	-1.303
32.0	2606	1960	9.77E-03	8.02E-03	-1.136	-1.424
35.0	2319	1724	8.70E-03	7.05E-03	-1.253	-1.552

Results for R5 reactor containing 75% S1 and 25% C1

Results for R6 reactor containing 75% S2 and 25% C1

Time	GC Area		Molar Conc.		ln(C/Co)	
(day)	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
0.0	8117	8140	3.01E-02	3.30E-02	0.000	0.000
0.4	8027	7860	3.08E-02	3.29E-02	-0.011	-0.035
0.9	7941	7622	3.09E-02	3.24E-02	-0.022	-0.066
1.9	7628	7085	3.01E-02	3.10E-02	-0.062	-0.139
3.9	7303	6454	2.93E-02	2.94E-02	-0.106	-0.232
4.9	7090	6189	2.81E-02	2.81E-02	-0.135	-0.274
5.9	6778	5914	2.69E-02	2.72E-02	-0.180	-0.319
7.9	6446	5512	2.51E-02	2.52E-02	-0.230	-0.390
8.9	6128	5189	2.52E-02	2.51E-02	-0.281	-0.450
9.9	5759	4850	2.38E-02	2.36E-02	-0.343	-0.518
10.9	5555	4640	2.31E-02	2.30E-02	-0.379	-0.562
12.9	5260	4330	2.17E-02	2.18E-02	-0.434	-0.631
13.9	4662	3807	2.12E-02	2.16E-02	-0.554	-0.760
15.9	4567	3693	2.00E-02	2.06E-02	-0.575	-0.790
16.9	3309	2676	1.91E-02	2.00E-02	-0.897	-1.113
22.0	3816	2988	1.77E-02	1.85E-02	-0.755	-1.002
24.0	3478	2700	1.70E-02	1.78E-02	-0.847	-1.104
26.0	3207	2474	1.68E-02	1.78E-02	-0.928	-1.191
29.0	2902	2211	1.54E-02	1.64E-02	-1.029	-1.303
32.0	2606	1960	1.47E-02	1.59E-02	-1.136	-1.424
35.0	2319	1724	1.36E-02	1.49E-02	-1.253	-1.552

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