SUSTAINABLE REUSE OF COAL FLY ASH TO MITIGATE LANDFILL METHANE

by

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Abstract

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Of the 130 million tons of coal combustion residuals (CCRs) generated annually in the US, around 40% percent is re-used, 12% is sent to municipal solid waste (MSW) landfills, and 48% is stored on-site by utilities (American Coal Ash Association, 2015; US Energy Information Administration, 2014). The US Environmental Protection Agency (EPA) has documented several hundred cases of heavy metals and other toxics from coal ash escaping from electric utility surface impoundments and damaging surface or ground water (Associated Press, 2014). In 2014 the EPA thus promulgated new rules to protect waterways near coal ash landfills and surface impoundments. The EPA Coal Ash Rule, although potentially helpful to water quality, will increase utilities' costs for managing CCRs on-site, and likely result in more CCRs being sent to MSW landfills. Thus, there is a critical need to find new ways of re-using ash in order to lower rule compliance costs for utilities, as well as to foster sustainable waste management.

Methane (CH_4) is a powerful greenhouse gas (GHG), contributing 32% of current climate forcing (US EPA, 2015). EPA has recently proposed rules to require additional landfills to install methane collection and control systems. However, much more remains to be done. EPA's new rules will reduce landfill CH_4 emissions by 487,400 tons per year, but US landfills currently emit 4.6 million tons of CH_4 per year (US EPA, 2015). 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 Class F 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. This would be particularly significant because increasing methane oxidation via aerobic mechanisms can be difficult, due to compaction requirements for final landfill covers that limit oxygen diffusion. Fly ash could also potentially serve as a methane adsorbent.

The current work is a preliminary study that examines the potential use of Class F fly ash (non- cementitious) in landfill covers to reduce emissions of methane. Eight laboratory scale reactors or columns were constructed which contained 2 types of soil, 2 kinds of fly ash and 4 combinations of fly ash/soil. The suitability of each of these combinations in columns was compared to determine which combination best assisted in methane removal. Since it was a preliminary study some of the actual landfill conditions were not simulated; for example, the soil and/ fly ash combination were not compacted, landfill gas was passed through the media at higher flow rates and oxygen was not present in the upper layers landfill cover soil. The results of the research show that fly ash containing higher percent of carbon aided in methane removal and the removal mechanism involved predominantly could be adsorption. Moreover, the recommendations provided for future research in this study need to be explored to determine the removal mechanisms involved and to improve methane removal by fly ash.

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Chapter 1

INTRODUCTION

1.1 Background

1.1.1   Coal Ash Waste Problem

Fossil fuels (coal, natural gas and petroleum) contribute nearly 67% of the electricity generated in the United States. Of these, coal alone is used to produce nearly 40% of the electricity, more than any other source (U.S. EIA, 2014). Further, coal combustion generates 110 million tons of coal combustion by-products (CCBs), or coal ash, per year. It is estimated that 52 million tons (47%) of CCBs is currently re-used, while the remaining 53% is stored on-site or sent to landfills.

On-site storage of coal ash has attracted a lot of attention due to its adverse economic and environmental impacts. US Environmental Protection Agency (EPA) lists more than 670 coal ash basins across the U.S. These storage basins have the potential to contaminate waterways and underground aquifers, due to heavy metals and other toxics. In fact the US Environmental Protection Agency (EPA) has documented 132 and 123 cases of heavy metals and other toxics from coal ash damaging surface waters and groundwater, respectively (American Coal Ash Association,2015). In 2008, a containment berm burst at a coal-fired power plant in Kingston, Tennessee, and released over 5 million cubic yards of coal ash into the Emory and Clinch rivers. Homes in the nearby community were destroyed, and the clean-up cost alone was estimated to be around $1.2 billion. In another incident in 2014, a drainage pipe below coal ash basins collapsed at a power plant in Eden, North Carolina, spilling 39,000 tons of ash into the Dan River, turning it gray for 70 miles (Associated Press, December 2014).

The growing concern about these issues found articulation in December 2014 when EPA issued new rules to protect waterways near coal ash storage facilities. Companies operating power plants with coal ash storage facilities needed to increase leak monitoring; control blowing dust; close storage areas that are structurally deficient or tainting waterways; and close storage sites not meeting the standards prescribed. Management costs for CCBs in the US are currently $30 per ton (Siddique, 2010). These new regulations, while helping protect waterways surrounding coal ash storage facilities, will increase CCB management costs for electric utilities. There is therefore a need to find innovative ways of re-using waste ash that can help lower these costs.

CCBs that are generated during electricity production from burning coal include several types of solid residues, such as bottom ash, fly ash, boiler slag, flue-gas desulfurization residues, and fluidized bed combustion ash. Fly ash is fine particulates captured by particulate control equipment. Bottom ash and boiler slag are coarser and heavier fractions that are collected at the bottom of the furnace. Bottom ash includes porous particles that fall from pulverized dry-bottom boilers, whereas boiler slag comes from pulverized wet-bottom boilers or cyclone boilers (Park, 2014; EPRI, 2009; Pflughoeft-Hasset et al., 1999). Coal fly ash is divided into two classes, F and C, by ASTM C 618. Class F fly ash is produced from burning anthracite and bituminous coals. Class C fly ash is produced from lignite and sub-bituminous coals. Class C fly ashes can contain significant amounts of calcium hydroxide and, therefore, can be self-cementing. Due to this property of Class C fly ash, it is typically used for construction purposes. (Palmer et al, 2000). Some of the uses of CCBs that do not require any prior government approval include construction and manufacture of products, hazardous waste stabilization, aggregate for roads, structural fill, controlled density or slurry fill among many others (NDEQ, 2004).

Beneficial re-use of CCBs throughout the world has been much researched (Pandey and Singh, 2010). CCBs have been widely studied in agricultural and engineering applications because of their pozzolanic and highly alkaline properties (Iyer and Scott, 2001; Kikuchi 1999). Fly ash which constitutes the largest percent (> 70%) of the CCBs has been used in large quantities and in wide range of applications (Siddique, 2010; Butalia and Wolfe, 2000). Fly ash has been utilized as a major component of blended cements (Naik et al., 1995a,b), a replacement for sand in manufacturing controlled low strength materials (Naik et al., 2001, 1990; Naik and Singh, 1997), a lightweight aggregate (Ramme et al., 1995; Courts, 1991; Hay and Dunstan, 1991), a road-base material (Takada 1995), an improvement for degraded soil due to improved nutritional and physico-chemical properties (Pandey and Singh, 2010), a low-cost adsorbent (Wang and Wu, 2006), and an adsorbent for waste management (Iyer and Scott, 2001). Ali et al (2009) conducted a study of three by-products (fly ash, phosphogypsum and blast furnace) for their potential re-use to reduce methane emissions resulting from rice cultivation. They reported that a fly ash amendment level of 10 Mg/ha reduced total seasonal CH_4 emissions by 20%, while increasing rice grain yields by 17%. Fly ash has an amorphous mixture of ferro-alumino-silicate minerals that contains a high amount of iron and manganese oxides. These may have acted as electron acceptors and thereby enhanced methane oxidation.

Despite its positive re-use in various applications stated above, more than 35 million tons of fly ash is still disposed of on-site by utilities or in landfills each year. From an integrated waste management perspective, fly ash is a valuable resource that has not yet been fully utilized and exploited. Various studies have focused on use of fly ash in conjunction with admixtures in the waste management industry, as a landfill bottom liner

or cover material (Cokca and Yilmaz, 2004; Mollamahmutoglu and Yilmaz, 2001; Prashanth et al., 2001; Nhan et al., 1996). Mollamahmutoglu and Yilmaz (2001) concluded that a 20% bentonite-fly ash mixture is suitable as a liner or cover material to achieve hydraulic conductivity k < 10^{-7} cm/sec. Cokca and Yilmaz (2004) reported that rubber and bentonite (up to 10%) added to fly ash appeared to be a suitable material for landfill liners, able to achieve the required conductivity (<10^{-7} cm/s). Prashanth et al. (2001) reported low permeability of 3 types of fly ash combined with various percentage of lime (0 to 15%), as a landfill liner material.

However, none of these previous studies has focused on fly ash applications in municipal solid waste (MSW) landfill final cover design to minimize methane emissions. Such an application would be mutually beneficial for all. Electric utilities would have a beneficial way to re-use their ash at no cost at all. Landfills would accept the ash for free as a material useful to them which would also allow them to reduce methane emissions. The cost of final covers can be substantial ($75,000 to $100,000 per acre). Thus, obtaining effective cover material for free would significantly benefit landfills.

1.1.2   Landfill Methane Problem

Despite increased rates of recycling, and combustion of waste to generate electricity, 53% of municipal solid waste (MSW) in the US was still landfilled in 2013. Generation of landfill gas (LFG), which is comprised of 50-55% methane (CH_4) and 40-45% carbon dioxide (CO_2), is one of the major environmental challenges associated with landfills (Scheutz et al., 2009a, b; Chiemchaisri et al., 2007). This landfill gas is produced by anaerobic decomposition of organic waste by microbes. CH_4 and CO_2 are greenhouse gases (GHG) with tremendous impact on global warming and climate change. However, CH_4 is a more powerful greenhouse gas with global warming potential 28 times that of

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CO_2 over 100 years. It currently contributes 32% of climate forcing, or heat-trapping (Intergovernmental Panel on Climate Change, Climate Change 2013). In March 2014, the White House released the "Strategy to Cut Methane Emissions" as part of President Obama's Climate Action Plan. Landfills are one of the 4 key economic sectors mentioned in the plan (Utech, 2014).

Landfills are the 3rd largest source of US human methane emissions. Figure 1-1 shows the primary sources of greenhouse gases in the US, in which landfills contribute 18% of the US total (USEPA, 2013).
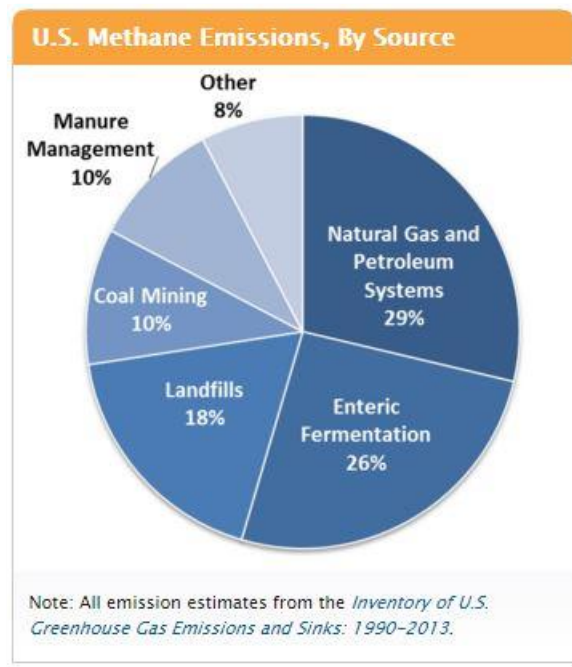
Figure 1-1 Primary sources of GHG in US (USEPA, 2013)

In response to a directive from the White House "Strategy to Cut Methane Emissions", EPA in August 2015 proposed updates to its 1996 Emission Guidelines for existing MSW landfills, and its New Source Performance Standards for new and modified landfills. These updates will require additional landfills to install landfill gas collection and control systems, reducing landfill methane emissions by 487,400 metric tons per year by 2025. More remains to be done, however, since landfills currently release 4.6 million metric tons of methane per year. Even when landfills capture methane and burn it to produce electricity, around 25% of methane still leaks through landfill covers (USEPA, 2013 and 2015).

1.2 Research Objectives

Conventional landfill covers are made from soil. Aerobic microbes (methanotrophs) in the soil typically oxidize 10-100% (average around 40%) of the methane passing through the cover to carbon dioxide (USEPA, 2005 and 2015; Chanton et al, 2009). Since carbon dioxide's global warming potential is 28 times less than that of methane, oxidation of methane in landfill contributes significantly in reducing greenhouse gas emissions in terms of CO_{2eq}.

Iron oxides, manganese oxides, nitrates, and sulfates have been shown to trigger microbial anaerobic oxidation of methane (AOM) in natural environments (Sivan et al., 2014). Adding Class F fly ash, which contain these components to the soil of a landfill cover, would therefore be expected to increase AOM in the lower layers of the cover. This would be particularly significant because increasing methane oxidation via aerobic mechanisms can be difficult due to compaction requirements for final landfill covers that limit oxygen diffusion. Fly ash may also potentially serve as a methane adsorbent. Fly

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ash incorporation in texturally variant soils modifies the soil physical physio-chemical environment which in turn may influence methane oxidation (Yunusa et al., 2006).

This project tests two kinds of Class F fly ash in combination with two kinds of soils taken from municipal solid waste landfills in lab column experiments. This was to determine the extent of methane removal assisted by fly ash when used as landfill cover for municipal solid waste. It also determines which type of soil and fly ash combination works best in assisting methane oxidation. It could thus provide a sustainable use of fly ash, mitigating the problem of its disposal, and reducing methane emissions in municipal solid waste landfills. This preliminary research of fly ash in landfill cover applications will greatly improve our understanding of opportunities for beneficial re-use of fly ash outside of the construction industry, specifically, in the field of solid waste management.

Chapter 2

Literature Review

2.1 Introduction

This chapter expounds the literature review on fly ash and its various uses, assessment of methane oxidation in various soils and methanotrophs and methanotrophic activity.

2.2 Fly ash and its uses

Fly ash is one of the coal combustion by-products consisting of fine, powdery particles predominantly spherical in shape, either solid or hollow, and mostly amorphous in nature. It is generally captured by electrostatic precipitators and other particle control equipment before the flue gases reach the stacks of coal-fired power plants. The four types of coal, viz. anthracite, bituminous, sub-bituminous, and lignite, vary in heating value, chemical composition, ash content and geological origin.

Depending upon the coal-bed makeup, the source of the coal being burned and techniques used for storage and handling, the composition of fly ash can vary considerably. However, all fly ash includes substantial amounts of silicon dioxide (SiO_2) (both amorphous and crystalline), aluminum oxide (Al_2O_3) and calcium oxide (CaO), the main mineral compounds in coal-bearing rock strata. The color of fly ash varies from gray to black, depending on the amount of un-burnt carbon in the ash. The burning of harder, older anthracite and bituminous coal typically produces Class F fly ash. This fly ash is pozzolanic in nature, and contains less than 7% lime (CaO).Possessing pozzolanic properties, the glassy silica and alumina of Class F fly ash requires a cementing agent, such as Portland cement, quicklime, or hydrated lime mixed with water to react and produce cementitious compounds.

Class C fly ash is produced from the burning of younger lignite or sub-bituminous coal. In addition to having pozzolanic properties, it also has some self-cementing properties. In the presence of water, Class C fly ash hardens and gets stronger over time. It generally contains more than 20% lime (CaO). Unlike Class F, self-cementing Class C fly ash does not require an activator. Alkali and sulfate (SO_4) contents are generally higher in Class C fly ashes.

There is a growing need to increase fly ash utilization due to the following:

i.   Adverse economic and environmental impacts associated with storage and disposal.

ii.   Increasing disposal costs.

iii.   Limited land reserved for disposal, thus enabling other uses of the land and decreasing disposal permitting requirements.

iv.   Potential financial returns from the sale of CCBs, or at least an offset of the processing and disposal costs.

v.   Replacement of non-renewable or expensive natural resources.

Throughout the world much research is being conducted on the use of fly ash. From the perspective of power generation, fly ash is a waste material, while from a coal utilization perspective, fly ash is a resource yet to be fully utilized. Figure 2-1 shows the possible uses of fly ash.
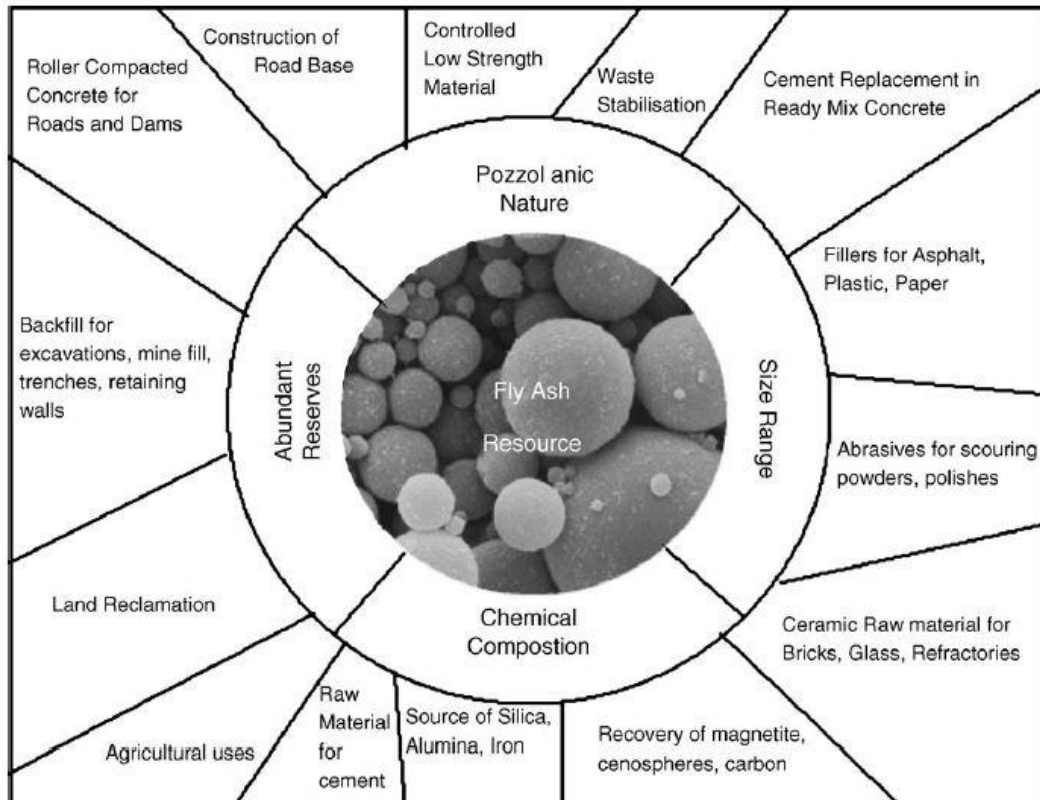
Figure 2-1 Uses of fly ash (Wang et al., 2006)

The physicochemical characteristics of fly ash, such as bulk density, particle size, porosity, water holding capacity, and surface area, make it suitable for use as an adsorbent. It is used as an adsorbent to clean flue gas from sulfur compounds, NO_x, mercury and gaseous organics. To reduce SO_x emissions, flue gas desulfurization (FGD) is often used. Whether it is sulfur compounds, NO_x, mercury or gaseous organics, activated carbon is generally used as adsorbent. However, it is very costly for large-scale environmental remediation applications. Coal fly ash is a cheap absorbent alternative. Fly ash recycling in the flue gas desulphurization process has shown promising results. A mixture of fly ash and calcium hydroxide for desulphurization has also been studied. It was found that $Ca(OH)_2$-fly ash mixtures were a low-cost SO_2 control option. The study

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also tested a process using activated carbon derived from fly ash for SO_2 and NO_x adsorption from industrial flue gas, which exhibited similar characteristics to typical activated carbon for flue gases (Davini, 2002). Figure 2-2 shows a schematic view of an FGD plant using coal ash.
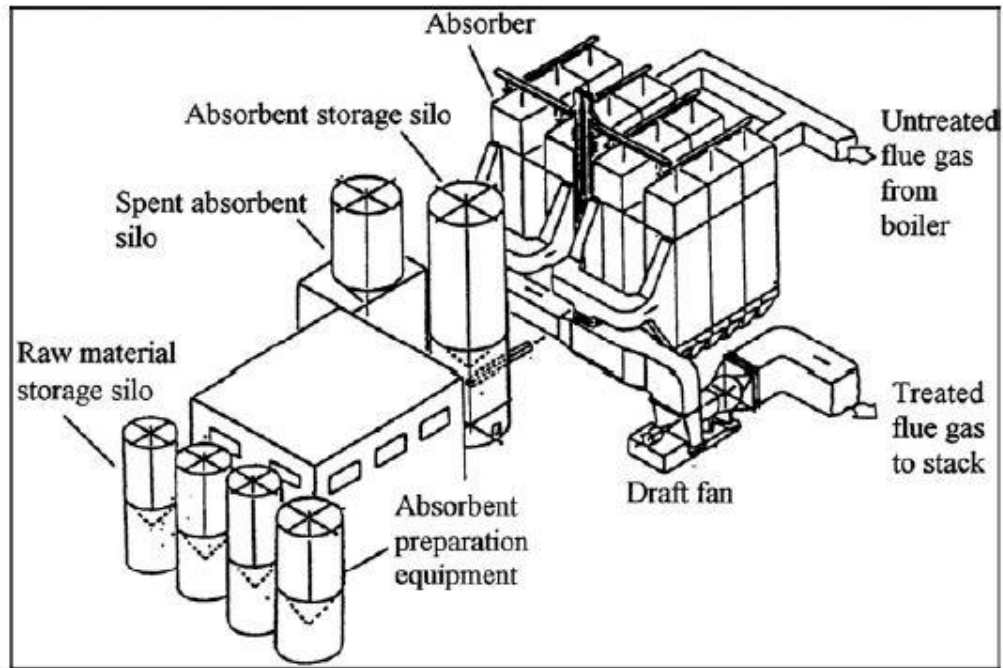
Figure 2-2 Schematic plant view of flue gas desulfurization using coal ash (Ngashima et al., 1993)

Fly ash has potential applications in wastewater treatment due to its major chemical components such as alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon, and its physical properties such as porosity, particle size distribution and surface area. Moreover, the alkaline nature of fly ash makes it a good neutralizing agent. Generally, in order to maximize metal adsorption by hydrous oxides, it is necessary to adjust the pH of wastewater using lime and sodium hydroxide (Ahmaruzzaman, 2009).

The cement industry also uses it as a raw material for the production of concrete. There are essentially three applications for fly ash in cement, including replacement of cement in Portland cement concrete, a pozzolanic material in the production of pozzolanic cements and a set retardant ingredient with cement as a replacement of gypsum. Cement is the most costly and energy intensive component of concrete. The unit cost of concrete is reduced by partial replacement of cement with fly ash. The utilization of fly ash is partly based on economic grounds, as pozzolana for partial replacement of cement, and partly because of its beneficial effects, such as lower water demand for similar workability, reduced bleeding, and lower evolution of heat. It has been used particularly in mass concrete applications and large volume placement to control expansion due to heat of hydration and also helps in reducing cracking at early ages. The major drawback of fiber-reinforced concrete is its low workability. To overcome this shortcoming, a material is needed which can improve the workability without comprising strength. The use of fly ash in concrete enhances the workability of concrete and is widely recommended as a partial replacement of cement. This also reduces the cost of construction. Fly ash concrete provides much strong and stable protective cover to the steel against natural weathering action. Because of the presence of cementitious compounds of calcium and a reactive glass, the high-calcium fly ash is quite suitable in Portland cement products. Several studies are being conducted to better understand the complexities of alkali aggregate reactivity and sulfate resistance with respect to fly ash in concrete (Ahmaruzzaman, 2009).

There are a number of reasons for the utilization of fly ash as a by-product aggregate in the manufacture of lightweight construction products. The main advantage is the economic savings to the manufacturer, associated with the reduced freight costs of shipping of the finished product, as compared to the non-light weight product when

weight is a factor. The reduced cost is especially noticeable when products such as bricks are considered. Fly ash bricks weigh, on average, one-third less than conventional clay-fired bricks (Reidelbach, 1970), enabling a truck to carry more bricks per load thereby reducing shipping costs and improving profit margins. The second economic reason is an abundance of low-cost fly ash available to make the bricks, yielding an excellent product. Pulverized fly ash brick at first instance may appear to be costlier than conventional products. However, ultimate financial benefit can be evaluated in terms of its improved physical and chemical properties. Depending on the type of soil, fly ash (20–50%) is used along with clay to produce clay bricks which are more porous (40– 50%) than fly ash bricks (20%), although clay-fly ash bricks have high strength and absorb less water than fly ash bricks (Ahmaruzzaman, 2009).

Fly ash has been used in embankment soil stabilization, sub-grade base course material, as aggregate filler, a bituminous pavement additive and as mineral filler for bituminous concrete. Fly ash used as a soil stabilizer along roadway embankments has been a beneficial practice for a number of reasons. In areas where burrow or fill and cover material are scarce, fly ash may be in plentiful supply from nearby electric power generation facilities. Ease of availability combined with positive physical properties can make fly ash soil stabilization cost effective. Shear strength is an important characteristic for soil stabilization fly ash utilization and it generally equals or exceeds the strength of soils typically used for embankments (FHWA, 1970; Lin, 1971). This strength is partially due to some fly ash having self-hardening or pozzolanic properties, which is a characteristic more common to class C fly ash and ash from atmospheric fluidized bed boilers.

Fly ash as a mine backfill has been demonstrated to be an attractive option for those plants located near the coal mine. Back-filling of underground mines is technically

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vulnerable and especially holds good potential for those areas where sand is scarce. Figure 2-3 shows use of CCBs for mine sites.
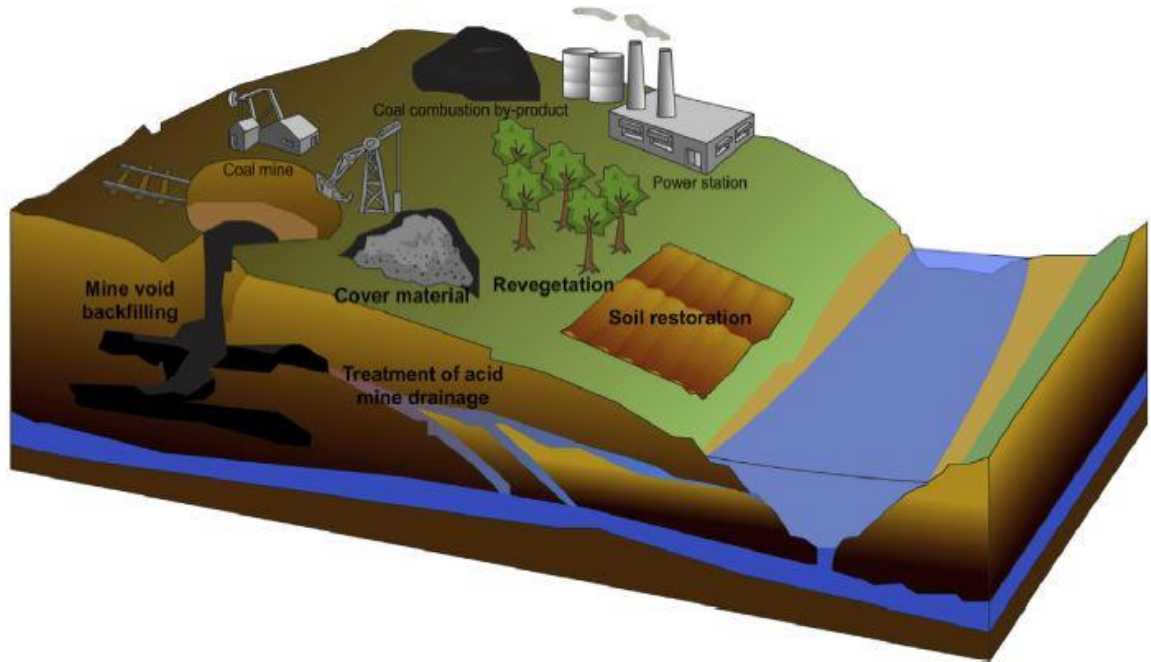
Figure 2-3 Use of CCBs for mine sites (Park et al., 2014)

In another study, blast furnace slag, fly ash and phosphogypsum (gypsum formed as a by-product of the production of fertilizer from phosphate rock) were tested for their economic feasibility at field level as good soil amendments in rice paddy soil to reduce methane emissions and increase rice productivity. Methane production results from the anaerobic decomposition of organic compounds, where CO_2 acts as inorganic electron acceptor. Microorganisms which are capable of reducing the energetically more favorable electron acceptors such as NO_3^-, Mn^{4+}, Fe^{3+} and SO_4^{2-} may outcompete those microorganisms (methanogens) using the less favorable electron acceptor such as CO_2 (Lovely et al., 2004). Therefore, CH_4 production was anticipated to decrease by supplying alternative electron acceptors like NO_3^-, Mn^{4+}, Fe^{3+} and SO_4^{2-},

which may result in a combination of inhibition effects and competitive effects with different microorganisms for the common electron donors (Achtnich et al., 1995; Jakobsen et al., 1981).

It has been recognized that iron oxide functions as a major oxidizing material and controls the production of organic acids (Asami and Takai, 1970) and CH_4 (Watanabe and Kimura, 1999) under submerged conditions. Although CH_4 emission was partially suppressed by the application of amorphous iron oxide in rice paddy soils (Asami and Takai, 1970; Yoshiba et al., 1996; Inubushi et al., 1997), this technique is not feasible at the field level due to the high cost of the amorphous iron oxide. Therefore the three previously mentioned materials were tested. Fly-ash, a by-product of the coal-burning industry, had already been recognized as a potential soil amendment to neutralize soil acidity and increase availability of mineral nutrients such as P, Ca, Mg, K, Mn, etc. for plant growth (Adriano et al., 1980; Lee et al., 2007). In addition, fly ash as an amorphous mixture of ferro – alumino –silicate minerals contains high amounts of iron and manganese oxides, which could act as electron acceptors and thereby, may suppress methane emissions during rice cultivation. Figure 2-4 shows the methane and carbon dioxide production activities with different levels of soil amendments applied (Ali et al., 2009).
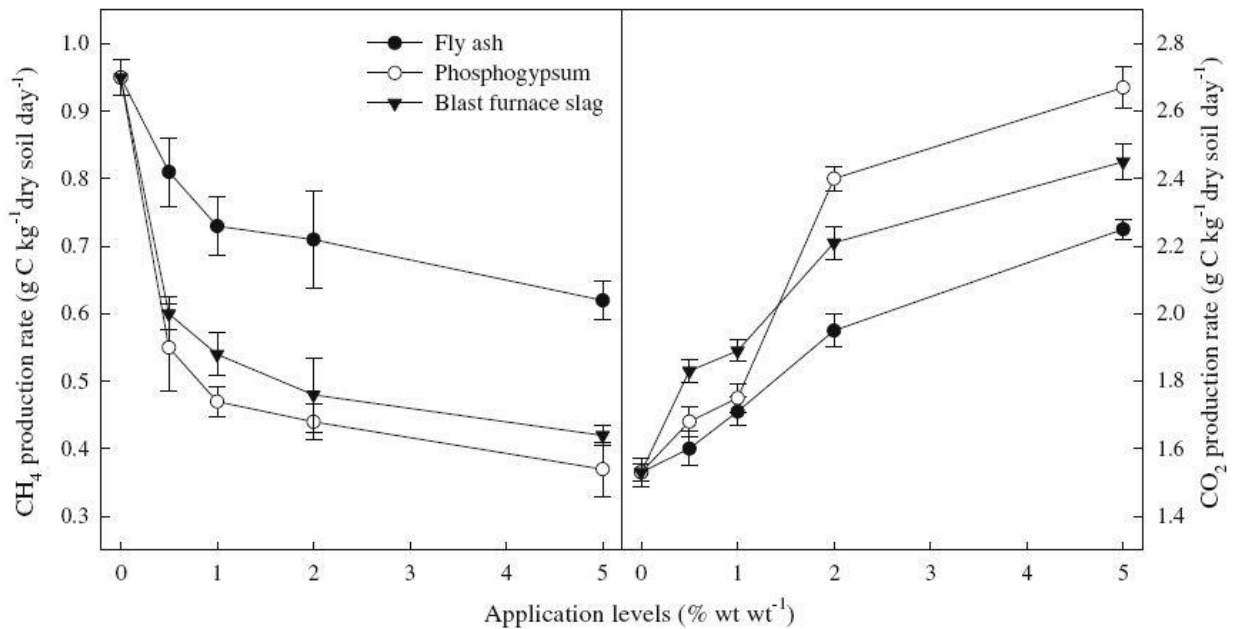
Figure 2-4 CH_4 and CO_2 production activities with different levels of soil

amendments applied (Ali et al., 2009)

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 10 Mg ha^{-1} fly ash

application, while increased rice yields by 17% over the control. This suppression of CH_4

emissions was attributed due to high concentrations of active iron, manganese

compounds, and sulfate in the selected amendments, which acted as electron acceptors

(Ali et al., 2009).

Another research has analyzed the impact of fly ash (FA) in soil systems in order

to improve physical, chemical and biological properties of degraded soils. It suggests that

FA could also be used as a source of readily available plant micro- and macro- nutrients.

Beneficial effects drawn from the research were that fly ash, (i) improves soil texture; (ii)

reduces bulk density of soil; (iii) improves water holding capacity; (iv) optimizes pH value; (v) increases soil buffering capacity; (vi) improves soil aeration, percolation and water retention in the treated zone (due to dominance of silt-size particles in FA); (vii) reduces crust formation; (viii) provides micro-nutrients like Fe, Zn, Cu, Mo, B etc.; (ix) provides macro-nutrients like K, P, Ca, etc.; (x) reduces the consumption of soil ameliorants (fertilizers, lime); (xi) FA can also be used as insecticidal purposes; (xii) decreases the metal mobility and availability in soil. However, recommendation for a large fly ash application to agricultural soils in a region cannot be made, unless extensive trials are made to find out a proper combination of FA with each type of soil to establish its quality and safety. Additionally, food-chain transfer studies for all potentially toxic elements present in FA are needed to evaluate the effect of heavy metal on the human health. Concurrently, in future, attention should be given on some important aspects related to FA incorporation to soil like long-term studies of impact of FA on soil quality, soil fertility, soil health and continuous monitoring on the properties of soil and FA (Pandey and Singh, 2009).

Palmer et al. (2000) conducted hydraulic conductivity tests in the laboratory and field to determine if mixtures of Class F fly ash and other materials such as Class C ash, sand, and bottom ash could be compacted to hydraulic conductivities less than 10^{-7} cm/s, which is the typical maximum permissible hydraulic conductivity for landfill liners. A test pad was constructed and tested to determine if the hydraulic conductivities found in the laboratory could be replicated in the field. Hydraulic conductivities less than 10^{-7} cm/s were not easily achieved in the laboratory. Various amounts of sand and Class C fly ash were added to reduce the hydraulic conductivity. Addition of 20–30% Class C fly ash reduced the hydraulic conductivity to near, but not below 10^{-7} cm/s, provided the compaction water content was greater than optimum water content. The design mixture

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and the mixture ultimately used in the field included a blend of Class C fly ash (38%) and equal parts (31% each) of bottom ash (as a substitute for sand) and Class F fly ash. Laboratory tests on these mixtures showed that hydraulic conductivity near or less than 10^{-7} cm/s could be obtained for compaction at optimum water content. However, constructing a fly ash liner with hydraulic conductivities similar to those found in the laboratory was difficult. The research recommended that careful consideration must be given to mixing, compaction, and lift interfaces so that macroscopic defects leading to high field hydraulic conductivity are avoided. Metal leaching (Cr and Se, in particular) must also be considered when designing a liner with fly ash.

In spite of a number of uses of fly ash and research done, more than 35 million tons of fly ash is still disposed of on-site by utilities or in landfills each year in US. Figure 2-5 and Figure 2-6 show fly ash production and utilization in different countries during 2005.
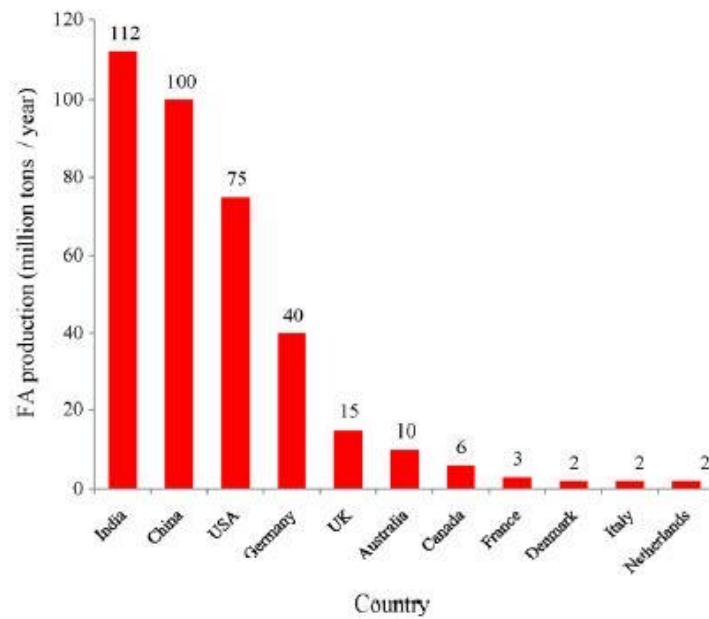
Figure 2-5 Fly ash production (million tones/year) in different countries in 2005 (Pandey and Singh, 2009)
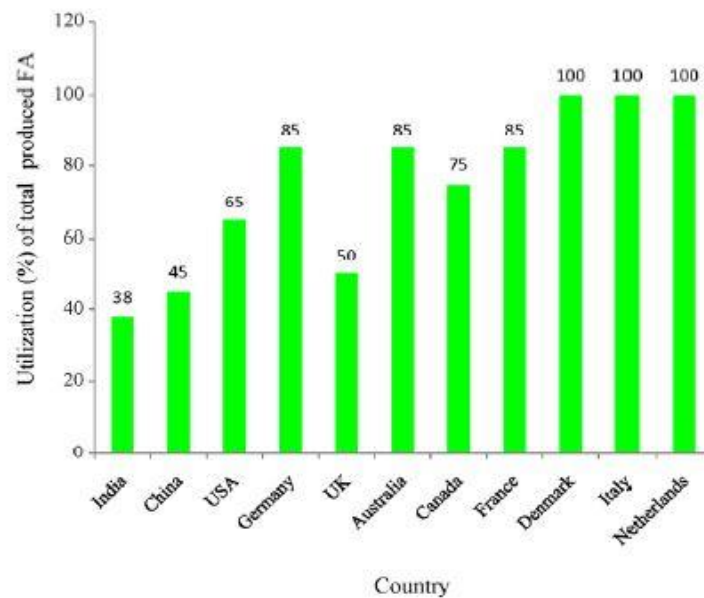
Figure 2-6 Fly ash utilization (million tones/year) in different countries in 2005 (Pandey and Singh, 2009)

2.3 Assessment of methane oxidation in soils

Landfills are among the largest anthropogenic methane sources worldwide, ranking third after agriculture (livestock farming and rice cultivation) and losses from fossil fuel distribution, processing and mining (Forster et al., 2007). Currently, it is estimated that annual global CH_4 emissions from landfills are in the range of 500–800 Mt CO_{2-eq}, representing the highest source of greenhouse gases within the waste sector, totaling <5% of overall global greenhouse gas emissions (Bogner et al., 2007).

According to the type of landfill operation technologies used, the amount of biodegradable waste disposed of, and the degradation conditions in the landfill, gas emissions are released at an environmentally relevant level over a time span of two to three decades, but even following landfill closure and capping gas emissions may continue to be manifested. Small emissions of gas are estimated to occur up to a period of 100 years. Contrary to methane, carbon dioxide formed inside landfills and released into the atmosphere produces a negligible effect on the environment due to its biogenic origin and the scarce quantities implicated compared to other human-related CO_2-sources (Huber-Humer et al., 2009).

The microbial oxidation of methane in engineered cover soils is considered a potent option for the mitigation of emissions from old landfills or sites containing wastes of low methane generation rates. Gerbert et al. (2010) show a laboratory column study conducted in order to derive design criteria that enable construction of an effective methane oxidizing cover from the range of soils that are available to the landfill operator. Therefore, the methane oxidation capacity of different soils was assessed under simulated landfill conditions. Five sandy potential landfill top cover materials with varying contents of silt and clay were investigated with respect to methane oxidation and

corresponding soil gas composition over a period of four months. Figure 2-7 shows the schematic set up of the column experiment.
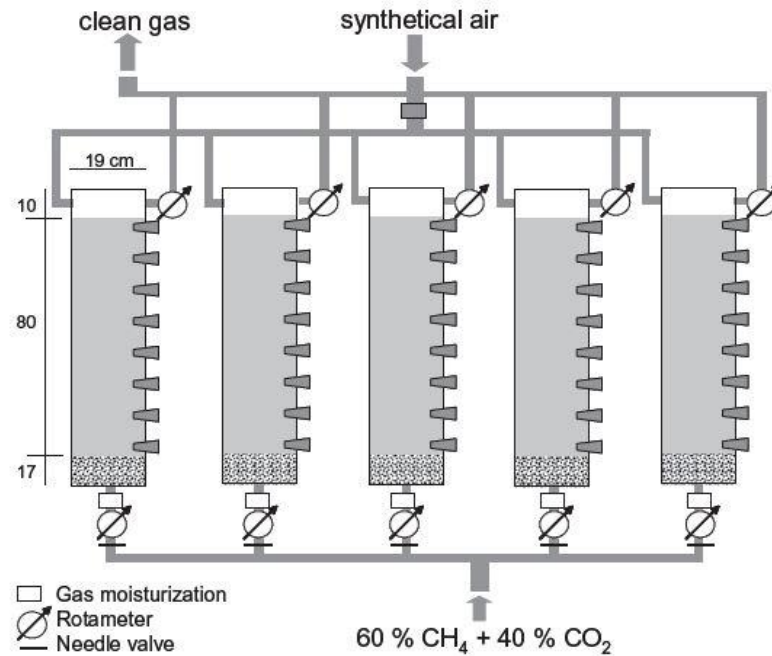
Figure 2-7 Schematic sketch of column experiment (Gerbert et al., 2010)

The soils were compacted to 95% of their specific proctor density, resulting in bulk densities of 1.4–1.7 g cm^{-3}, reflecting considerably unfavorable conditions for methane oxidation due to reduced air-filled porosity. The soil water content was adjusted to field capacity, resulting in water contents ranging from 16.2 to 48.5 vol. %. The investigated inlet fluxes ranged from 25 to about 100 g CH4 m^{-2} d^{-1}, covering the methane load proposed to allow for complete oxidation in landfill covers under Western European climate conditions and hence being suggested as a criterion for release from aftercare. The vertical distribution of gas concentrations, methane flux balances as well as stable carbon isotope studies allowed for clear process identifications. Higher inlet fluxes led to

a reduction of the aerated zone, an increase in the absolute methane oxidation rate and a decline of the relative proportion of oxidized methane.

For each material, a specific maximum oxidation rate was determined, which varied between 20 and 95 g CH_4 m^{-2} d^{-1} and which was positively correlated to the air-filled porosity of the soil. Methane oxidation efficiencies and gas profile data imply a strong link between oxidation capacity and diffusive ingress of atmospheric air.
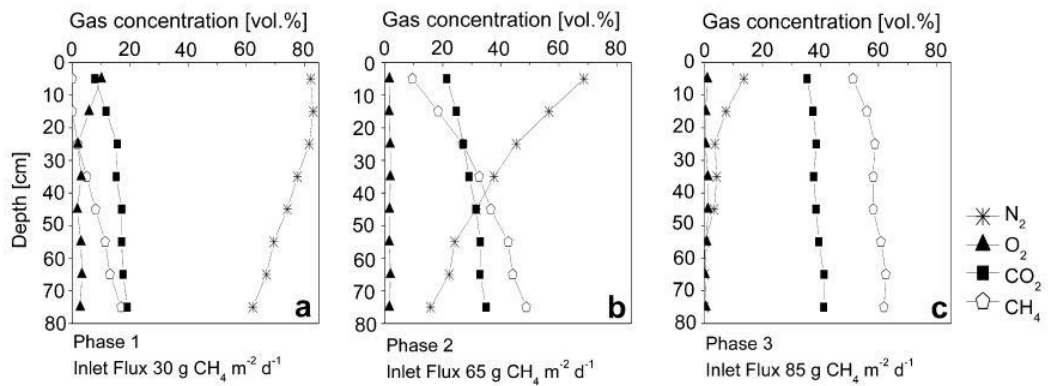
Figure 2-8 Column 1 gas profiles (Gerbert et al., 2010)
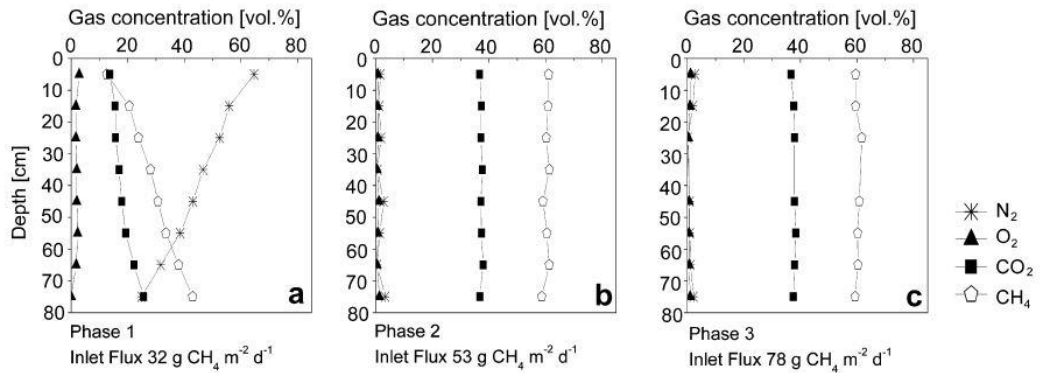
Figure 2-9 Column 5 gas profiles (Gerbert et al., 2010)

For column 5 with elevated levels of fine particles and high organic matter content, methane production impeded the quantification of methane oxidation potentials.

The relationship between inlet methane fluxes and the absolute methane oxidation rates for all measured values is shown in Figure 2-10.
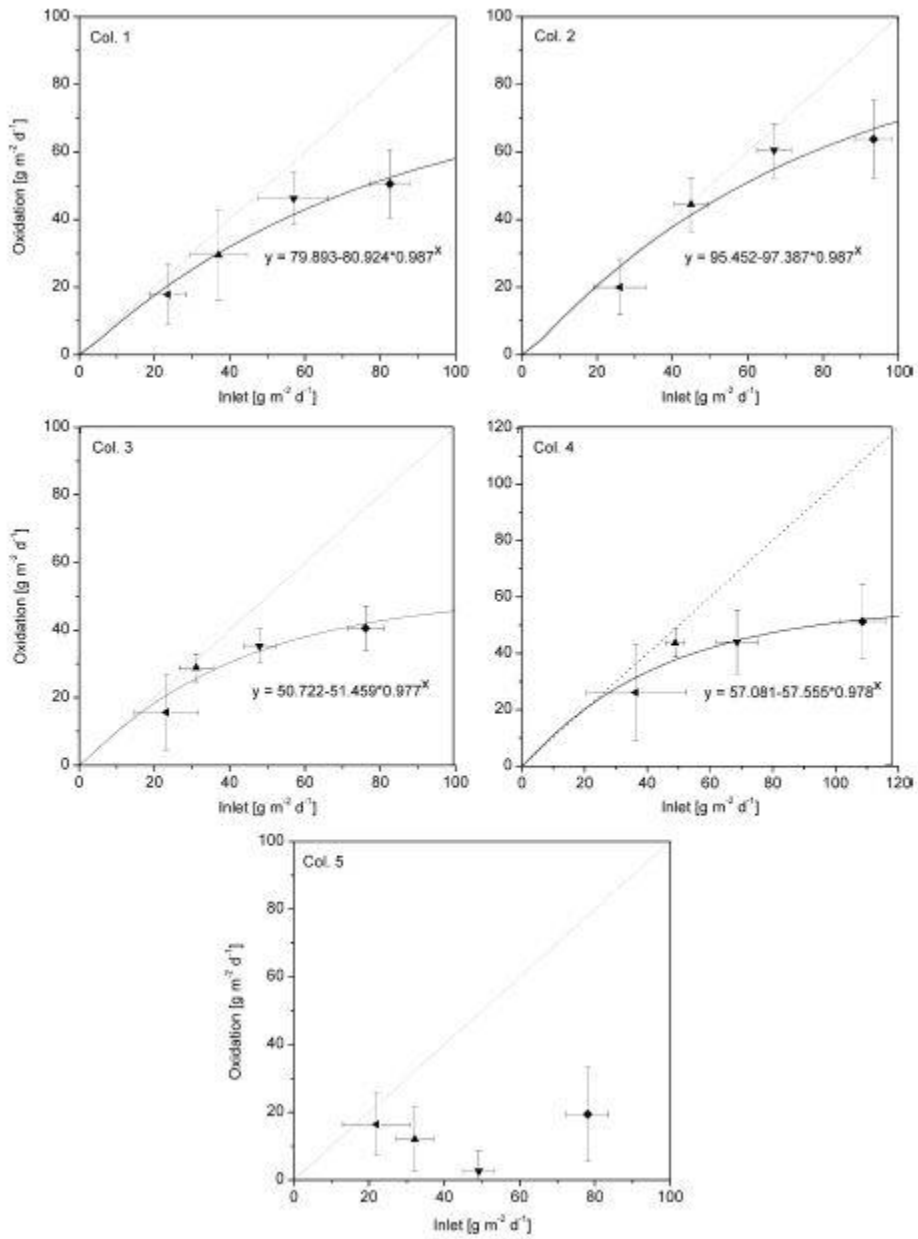
Figure 2-10 Absolute methane oxidation rates (Gerbert et al., 2010)

Except for column 5, all columns showed increasing absolute removal rates with increasing methane influx rates up to a column-specific maximum (OR_{max}). Column 2 had the highest oxidation rate, followed by columns 1, 4 and 3. For column 5, no extrapolation was possible. Regarding the design of landfill cover layers, it was concluded that the magnitude of the expected methane load, the texture and expected compaction of the cover material are key variables that need to be known. Based on these, a column study can serve as an appropriate testing system to determine the methane oxidation capacity of a soil intended as landfill cover material.

2.4 Methanotrophs and methanotrophic activity

Methanotrophs are gram-negative bacteria that use CH_4 to gain energy and carbon for their growth (Hansen et al, 1996). These bacteria are important regulators of CH_4 fluxes from the biosphere to the atmosphere, for example landfills, where CH_4, one of the most important greenhouse gases, is produced in large quantities (Reeburgh, 1996).

There are two main groups of methanotrophic bacteria, which are designated type I and type II (Hansen et al., 1996; Bowman, 2000). Type I methanotrophs (including two genera named type X) utilize the ribulose monophosphate pathway as the primary pathway for carbon assimilation, while type II methanothrophs use the serine pathway. They also differ in morphology. Phylogenetic studies of 5S rRNA and 16S rRNA have confirmed the distinction between type I and type II methanotrophs and have placed them, respectively, in the ɣ and α subdivisions of the Proteobacteria (Bowman, 2000; Bratina et al., 1992). New genera, that are phylogenetically related to type II, have recently been discovered in an acidic peat bog (Dedysh et al., 2002), but it is not yet known how common this group of bacteria is in non-acidic environments. It has been

observed that shifts in the methanotroph populations in soils can occur in response to environmental stimuli such as changes in concentrations of CH_4 and O_2, temperature, pH and nitrogen sources (Hansen et al, 1996).

Furthermore, several studies have indicated that type I and type II methanotrophs seem to occupy different niches. For instance, type I strains are likely to dominate in nutrient-rich environments (Graham et al., 1993; Amaral et al., 1995; Börjesson et al, 1998), which agrees with the finding that nitrogen fixation is more common in type II methanotrophs (Auman et al., 2001). The primary objective of the research was to determine whether the two types of methanotrophs could be linked to activities at specific temperatures. Temperature is of the utmost importance for the ability of the methanotroph community to oxidize CH_4, and a better understanding of the optimal conditions for oxidation would improve predictions of oxidation rates and would also help in the construction of better landfill covers, biofilters, etc. In this respect, it has been shown that the analysis of phospholipid fatty acids (PLFAs) can provide a quantitative measure of the bacterial and eukaryotic biomass in environmental samples (Pinkart et al., 2002). Many strains of the two main types of methanotrophs have been found to produce large amounts of unusual fatty acids (Bowman, 2000; Wise et al., 1999); hence these fatty acids can be used as biomarkers. *Methylomonas* is a type I methanotroph whereas *Methylocystis* and *Methylosinus* are exclusively in the type II genera.

Methanotrophs are aerobic microorganisms that use oxygen to oxidize CH_4 to CO_2 and biomass (Hanson and Hanson, 1996). Methanotrophs oxidize methane to methanol using the enzyme, methane monooxygenase (MMO). There are two distinct forms of MMO: the particulate membrane-bound form (pMMO) and the soluble form, sMMO. The *pmoA* is a functional gene encoding the active site subunit of pMMO for all known methanotrophs (Lieberman and Rosenzweig, 2004), with the possible exception of

members of the genus Methylocella, which are generally isolated from acidic

environments (Dunfield et al., 2003; Theisen et al., 2005). The *pmoA* gene has been

used as a marker in molecular techniques to target methane-oxidizing bacteria in

different environments (Kolb et al., 2003; Pester et al., 2004), including landfill cover soil

(Cebron et al., 2007). According to Gebert et al. (2003), methanotrophs develop better in

the upper layers where there is an optimum supply of oxygen. Therefore, it is likely that

the difficulty of O_2 diffusing into the deepest layers is one of the primary factors resulting

in low methanotrophic bacterial development in these zones.

Factors such as CH_4/O_2 mixing ratio, soil moisture content, temperature, soil pH,

and soil type affect microbial methane oxidation in landfill covers. The CH_4/O_2 mixing

ratio plays a critical role in controlling oxidation activity of methanotrophs (Hrad et al.,

2012). Based on the stoichiometric equation, two moles of oxygen are required to oxidize

one mole of methane. According to biochemical kinetics for CH_4 oxidation by

methanotrophs, an O_2/CH_4 ratio of 3:1 is necessary to efficiently oxidize CH_4 (Yamini and

Reddy, 2014). He et al. (2011) reported that ambient oxygen concentrations of 20%,

typical of ambient air, were favorable for CH_4 oxidation; ratios less than 3% negatively

impact the microbial oxidation rate of landfills (He et al., 2012).

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 CH_4 oxidation (Chanton et al., 2011a, b;

Spokas and Bogner, 2011). Boeckx et al. (1996) reported that the optimal oxidation water

content ranged between 15.6 and 18.8% w/w. Rachor et al. (2011) performed a lab study

on different soils where the moisture content was adjusted to the field capacity, resulting

in 16.2 to 48.5% vol. Park et al. (2009) reported the optimum moisture content for methane oxidation was in the range of 10-15% by weight.

Methane oxidation rate typically increases with an increase in temperature. Lower temperatures cause bacterial 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 (Spokas and Bogner, 2011; Park et al., 2009; Borjesson et al. 2004). Czepiel et al. (1996) reported that oxidation stops when the temperature reaches at 45°C.

The optimum soil pH for CH_4oxidation ranges from 5.5-8.5. Since methanotrophs have the capacity to adapt to a wide range of pH, this is not a major limiting factor for microbial methane oxidation (Scheutz et al., 2009a, b).

Type of soil also affects methane oxidation capacity. Rachor et al. (2011) assessed methane oxidation capacity of different soils in a column study. They concluded that pore volume available for gas transport is of vital importance for the extent of microbial methane oxidation. They reported that soils intended for enhanced methane oxidation should be compacted to the least possible extent and suggested that a more coarsely textured soil which retains higher air capacity while offering sufficient field capacity (e.g. a fine, loamy or silty sand) is preferable. Furthermore, they addressed that in spite of high compaction rates, most of the tested soil materials showed notable methane oxidation up to 50 g $CH_4/m^2/d$ fluxes. Gebert et al. (2010) reported that effective diffusion coefficient governing oxygen migration through soil is exponentially related to air-filled porosity space and can be significantly decreased by degree of compaction. They reported that at a low degree of compaction (75% of the proctor density), a flux of

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3.5 g $CH_4/m^2/hr$ could fully be oxidized at all times by sandy loam. They suggested the soil's air-filled porosity of at least 14% vol. for methane oxidation.

The amount of inorganic N present in the landfill cover soil also affects its CH_4 oxidation rate. Methanotrophs have a high N-demand, so for every mole of carbon assimilated, 0.25 mol of N is used. However, the study conducted by He et al. (2011) reported that NH_4 addition did not have a significant impact on CH_4 oxidation compared to water content and O_2 concentration.

Chapter 3

Methodology

3.1 Experimental design

A laboratory column study was conducted to analyze the methane oxidizing capability of fly ash under simulated landfill conditions. Two types of soils having high plasticity and low plasticity designated as S1 and S2, respectively, were used. The two types of soils were obtained from two different sites at City of Denton landfill. Two types of Class F fly ash from two coal-fired plants designated as F1 and F2 were obtained. The names of the plants will not be provided, due to confidentiality reasons.

Table 3-1 shows the experimental design, consisting of 8 reactor columns to investigate the impact of fly ash vs. soil and fly ash/soil combinations on methane oxidation at constant moisture content of 15%.

Table 3-1 Experimental design

Column	Barrier Layer
1	S1
2	S2
3	70% S2 + 30% F1
4	70% S1 + 30% F1
5	70% S1 + 30% F2
6	70% S2 + 30% F2
7	F2
8	F1

3.2 Preliminary soil tests

Sieve analysis and Atterberg limits tests were conducted for the two soil samples. Both mechanical or sieve analysis and hydrometer method were performed to determine the distribution of coarse and fine particles contained within the soil. Atterberg limits test was performed to determine the plastic and liquid limits of the soil. The standard procedures were followed as provided in ASTM D 422 – Standard Test Method for Particle-Size Analysis of soils and ASTM D 4318 - Standard Test Method for Liquid Limit, Plastic Limit, and Plasticity Index of Soils.

3.3 Construction and setting up of reactors

Eight columns were constructed from plexiglass (acrylic plastic), each having length 35 inches, inner diameter 8.25 inches and a wall thickness 0.5 inch. Figure 3-1 shows a plexiglass column used in the experiment.
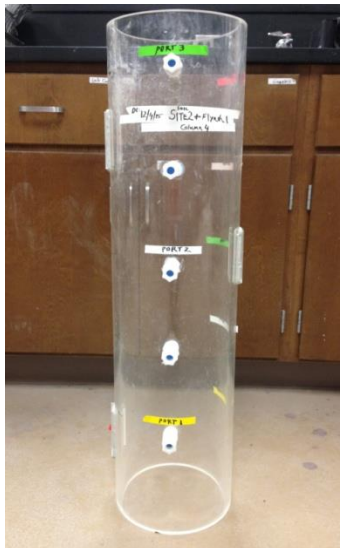
Figure 3-1 Plexiglass column

The columns were closed with sealing caps or plates at both ends. The sealing plates were squares with length of 12 inches and thickness 0.75 inches. Figure 3-2 shows the sealing plates used at both ends of the column.
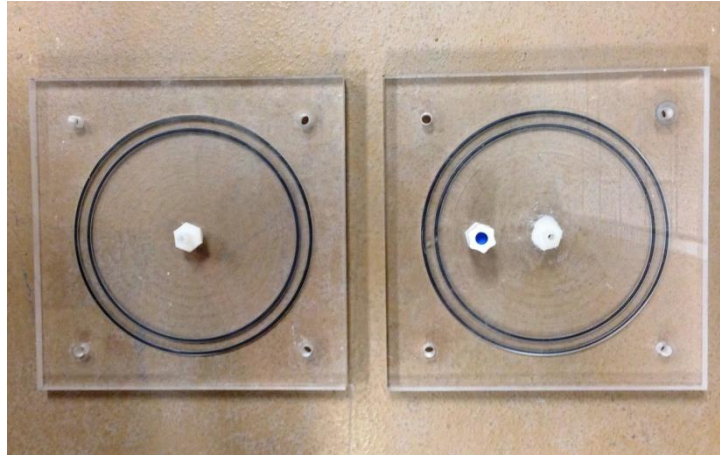
Figure 3-2 Bottom sealing plate (left) and top sealing plate (right)

As shown in the figure above, two circular grooves 1/8 inches by 1/16 inches were carved on the sealing plates for insertion of O-rings to guarantee air tight fit. The inner diameters of smaller and larger O-ring grooves were 8 inches and 9 inches, respectively. A half-inch hole was cut at the center of the plates, to which inlet and outlet tubes were attached. 3/8 inch diameter holes were drilled at the four edges of the sealing plate to insert coarse thread, 16 threads per inch, 3/8 inch diameter steel rods. The steel rods went through the sealing plates on which the columns were mounted and made to stand. Port holes on the columns, rod holes and tube fittings on the end plates and moisture port caps were designed using AutoCAD. The columns were then given to the machine shop to be cut as per the AutoCAD drawings. Figure 3-3 shows the height of methane ports on the column from ground level.
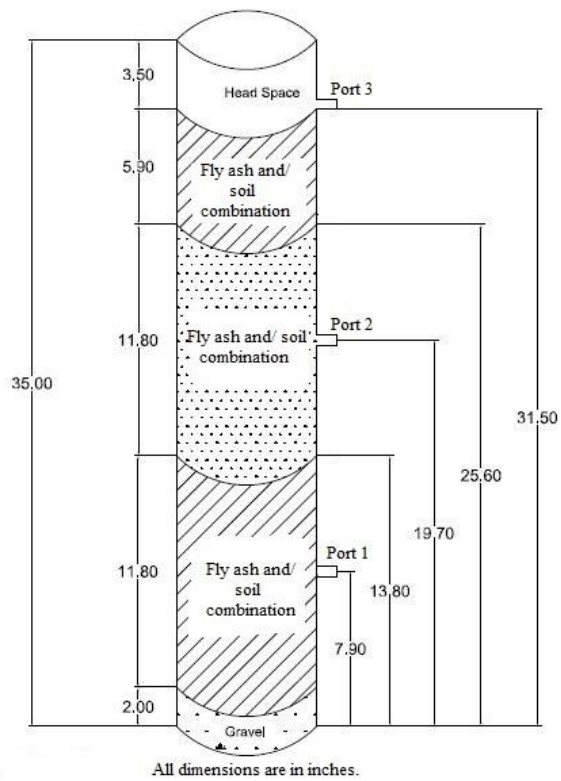
Figure 3-3 Methane ports on column

Figure 3-4 and 3-5 show the sketches of the moisture ports on column and moisture caps

drawn using software.
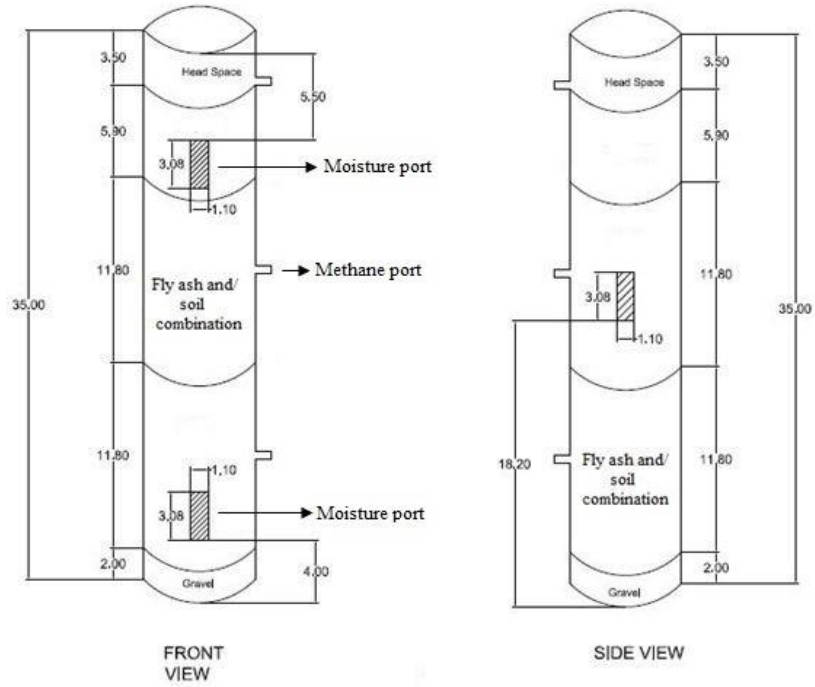
Figure 3-4 Front view and side view of column showing moisture and methane ports
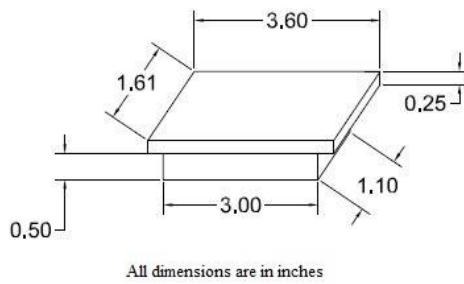
Figure 3-5 Sketch of moisture cap to seal moisture ports

A flow meter panel was built for proper organization and smooth running of the experiment. 16 Matheson flow meters reading up to 150ml/min were mounted on a PVC sheet to make the flow meter control panel. The bottom eight flow meters only were used - one for each column. The others were installed for possible future use. To ensure even pressure into the flow meters, a manifold was built such that the gas would go into the manifold first before entering the flow meters. The manifold consisted of large thick tubing capped at the ends with equidistant threaded holes drilled to attach the pipe tubing. The holes were drilled equidistant on the manifold to equalize the flow. Figure 3-6 shows the front and rear view of the flow meter panel.
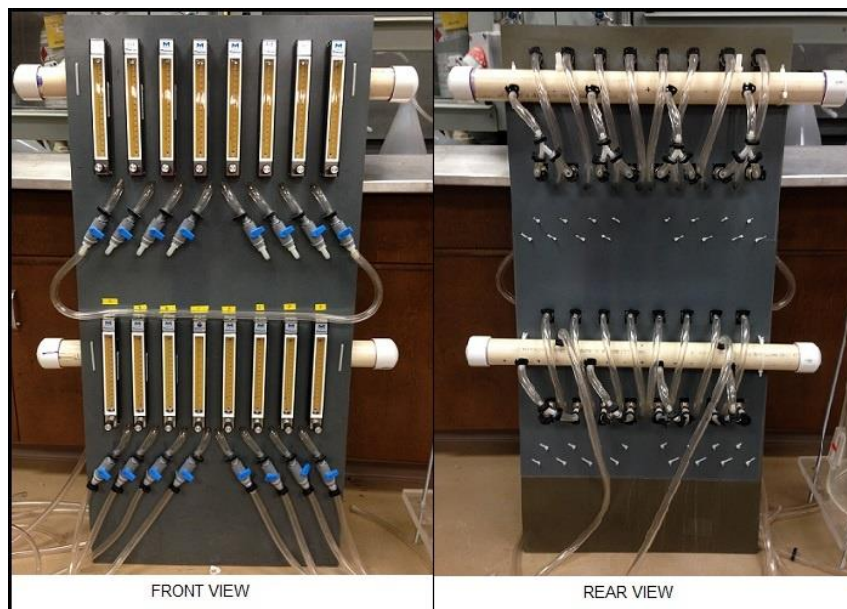
Figure 3-6 Front and rear view of the flow meter panel

The miniature PVC high flow ball valves, incline ¼ inch NPT female with 3/8 inch to 5/8 inch barb present below the flow meters were used to turn on and off the gas and to prevent loss of gas to the atmosphere when only few columns were running. The custom-made flow meter panel was thus easy to control and suitable for different requirements.

The water bubblers or humidifiers were made out of side arm flasks, a rubber stopper and tubing cut at an angle so as not to hinder gas flow. Figure 3-7 shows the humidifier set-up used.

Figure 3-7 Humidifier set up

The methane ports were made of ½ inch NPT compression fittings with 17 mm septa inserted in between the fittings to ensure a tight seal. Figure 3-8 shows the components of methane port and their assembled product. The assembled compression fittings were then screwed into the threaded holes on the column and sealed using sealant.

Figure 3-8 Compressions fittings for methane port (left) and assembled methane port (right)

The connections on the sealing caps to which the inlet and outlet tubes were attached, were made of barbed fittings. Figure 3-10 shows barbed fitting and compression fitting.

Figure 3-9 Compression fitting (left) and barbed fitting (right)

The entire set up was connected with 3/8 inch (inside diameter), chemical resistant, tygon PVC tubing.

A reactor or column was set up by first threading a washer and a screw on to each of the four steel rods. The base sealing plate with O-rings inserted into the grooves was then inserted through the steel rods such that the base plate stood at 4 inches from the ground surface as shown in Figure 3-10 (a). Fiberglass window screens roughly cut into 8 inches diameter were placed at the center of the base sealing plate as shown in Figure 3-10 (b). This was done to prevent the gravel, soil and/ fly ash from falling into the tubing. The cylindrical column was then mounted securely on the base plate such that they fit perfectly, as shown in Figure 3-10 (c).

Figure 3-10(a) Steel rods inserted through base plate (left);
(b) circular fiberglass window screen (middle);
(c) Column mounted on base plate (right)

Figure 3-10 (a) Steel rods inserted through base plate (left); (b) Circular fiberglass window screen (middle); (c) Column mounted on base plate (right)

Starting from bottom up, the column was then packed with 2 inches of coarse gravel as a distribution layer. Soil to be used was previously dried in the oven for 24 hours at 100^0C. The soil was then crushed in a crusher. The column was marked with a marker at 6, 18 and 24 inches from the top of the gravel layer. The first 6 inches from the gravel layer was considered as first layer, next 12 inches as second layer and last 12 inches third layer. As per the experimental design, the soil and/ fly ash mixture was mixed with 15% water in a tray. At a time, 6 kg of soil was taken and weighed for columns containing only soil and 15% water was added by weight. For columns with soil and fly ash mixtures, at a time, 5.6 kg of soil was mixed with 2.4 kg of fly ash (70% soil and 30% fly ash) and 15% water was added by weight. The mixture was thoroughly mixed to make it uniformly wet. The mixture was then covered and kept aside for a few minutes for the water to penetrate in case there were any dry areas left in the mixture. Figure 3-11 shows soil, fly ash and water mixture in a tray.

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Figure 3-11 Mixture of fly ash, soil and water

The large lumps of soil were roughly separated by hand and placed uniformly on the column. The soil mixture was lightly pressed or compacted with the palm of hand uniformly on all sides of the column. This method was continued till only the last 6 inches of the third layer on top remained to be filled. As the last 6 inches was considered as top soil, the soil mixture was uniformly placed on the column without any hand compaction. Once the column was filled with the soil mixture, the top sealing plate was immediately placed to seal the column and prevent any loss of moisture from the soil mixture. The top plate was then tightly fixed with washers and screws, as shown in Figure 3-12. Flattening of the O-rings uniformly after the top sealing plate was screwed tight suggested air-tight sealing.

Figure 3-12 Sealing the column with top sealing plate

Figure 3-13 shows the schematic diagram of the experiment.
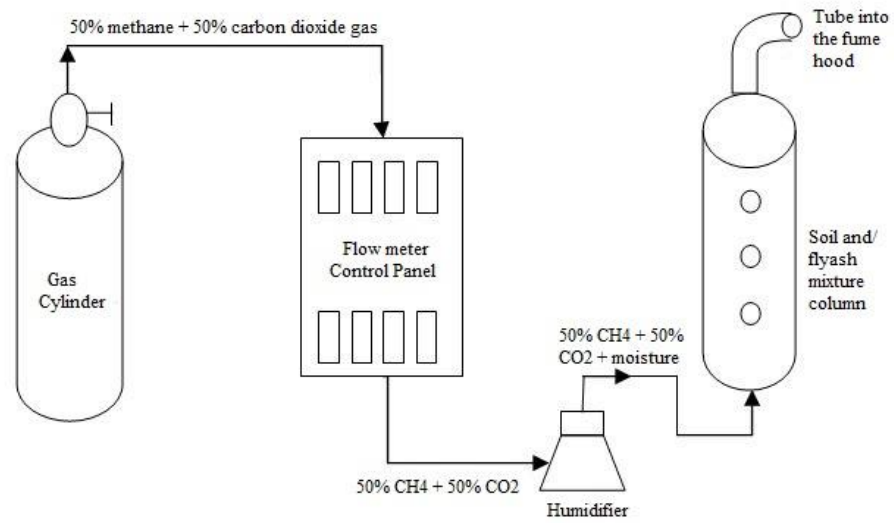
Figure 3-13 Simplified schematic sketch of the experimental set up

Figure 3-14 Experimental set-up

The gas cylinder contained synthetic landfill gas mixture of 50% methane and 50% carbon dioxide, which was let out of the cylinder at an output pressure of 25psi. The flow meters were adjusted to 80 ml/min. The gas mixture exiting the flow meters was then passed through the 8 humidifiers (1 humidifier for each column) containing 1 liter water each. The moist synthetic landfill gas exiting the humidifiers entered the column. All the columns were exposed to the synthetic gas mixture for a week before the starting the data collection to allow for system equilibrium and activation of the methanotrophic community.

3.4 Data collection and monitoring

The methane was measured at 3 ports present at 6 inches, 12 inches and 24 inches from the gravel layer using an International Sensor IQ – 350 EAGLE portable monitor.
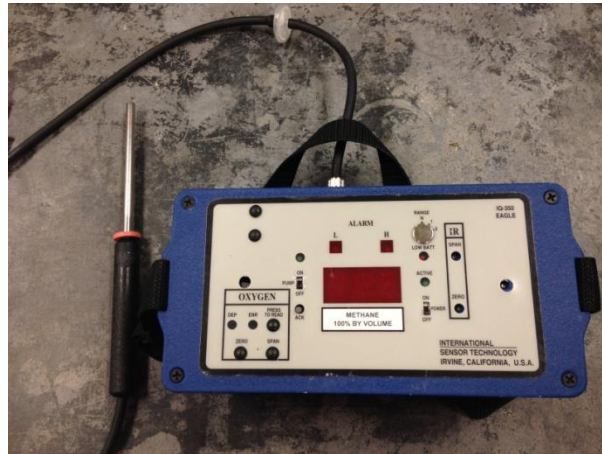
Figure 3-15 International Sensor IQ – 350 EAGLE portable monitor

The moisture was measured using a moisture probe – a Field Scout TDR 100 System. It read volumetric moisture content.

Figure 3-16 Moisture probe
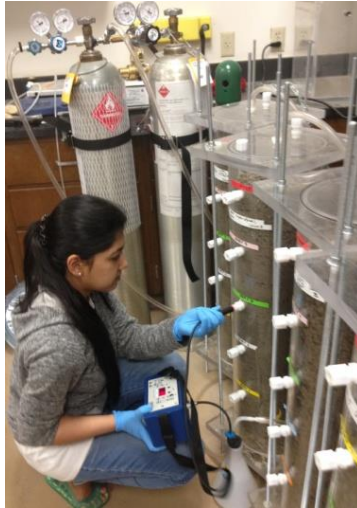
Figure 3-17 Methane data collection using International Sensor

Data was collected every 24 hours and recorded. However, moisture was measured only for 2 weeks as there was leakage of gas at the moisture ports. The moisture ports were thereafter sealed completely using clay putty.

The findings and data recorded are discussed in the next chapter.

Chapter 4

Results and Discussion

This chapter contains the results obtained from the preliminary soil tests and column experiments conducted. The results have been analyzed and discussed to evaluate the effect of fly ash on mitigating methane emissions.

4.1 Preliminary soil test results

Tables 4-1 and 4-2 show the grain-size distribution obtained from the dry sieve analysis of soils S1 and S2, respectively. Sieve and hydrometer analysis of soils S1 and S2 were plotted on semi-logarithmic graph with the grain size on a log scale and percent finer on a natural scale. Figure 4-1 shows the grain-size distribution plot for the calculations shown in Table 4-1 for S1 soil. Figure 4-2 shows the grain-size distribution plot for the calculations shown in Table 4-2 for S2 soil.

Table 4-1 Grain-size distribution for soil S1

Sieve No	Sieve size (mm)	Mass retained on each sieve (kg)	% of mass retained on each sieve (R_n)	Cumulative % Retained ($\sum R_n$)	% Finer
4	4.75	0.001	8.33	8.33	91.67
8	2.36	0.001	8.33	16.67	83.33
16	1.18	0	0	16.67	83.33
30	0.6	0.001	8.33	24.99	75.01
40	0.425	0	0	24.99	75.01
50	0.3	0	0	24.99	75.01
100	0.15	0.002	16.67	41.66	58.34
200	0.075	0.005	41.67	83.33	16.67
pan		0			
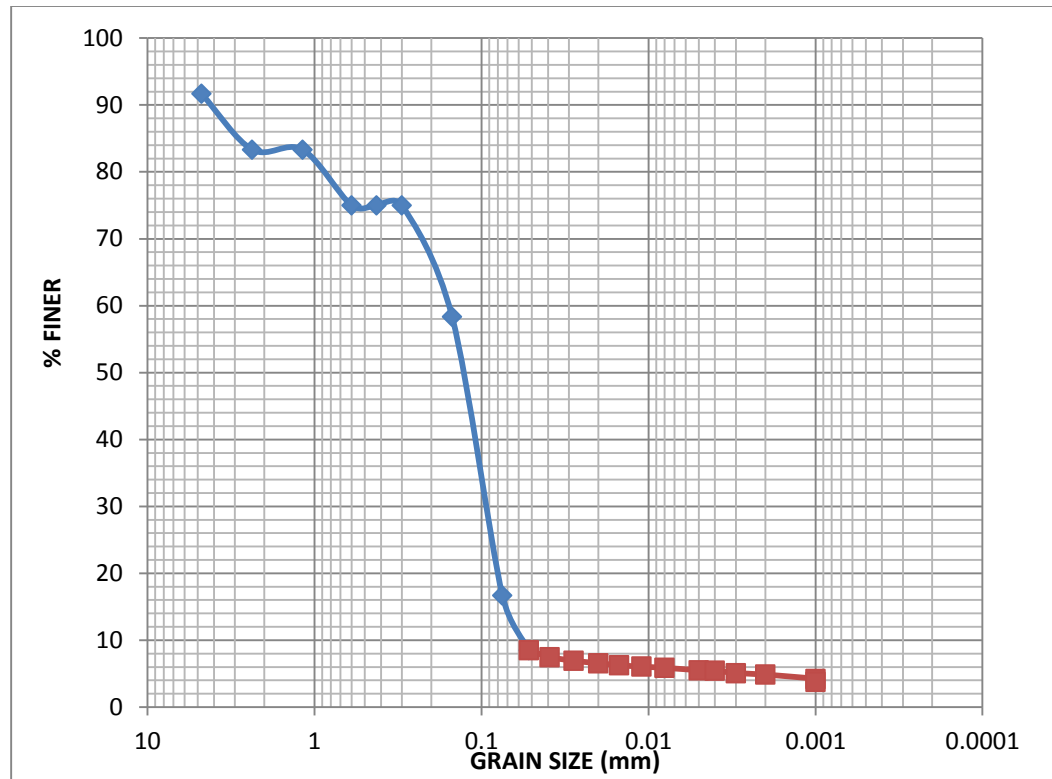
Figure 4-1 Plot of percent finer vs. grain size for Soil S1

Table 4-2 Grain-size distribution for soil S2

Sieve No	Sieve size (mm)	Mass retained on each sieve (kg)	% of mass retained on each sieve (R_n)	Cumulative % Retained ($\sum R_n$)	% Finer
4	4.75	0.001	1.350	1.35	98.65
8	2.36	0	0.000	1.35	98.65
16	1.18	0.001	1.351	2.7	97.3
30	0.6	0.001	1.351	4.05	95.95
40	0.425	0	0.000	4.05	95.95
50	0.3	0	0.000	4.05	95.95
100	0.15	0.006	8.108	12.16	87.84
200	0.075	0.06	81.081	93.24	6.76
pan		0			

Figure 4-2 Plot of percent finer vs. grain size for soil S2

The liquid and plastic limit calculations for soil S1 are shown in Table 4-3.

Table 4-3 LL and PL calculation for soil S1

Liquid Limit Determination	
Mass of empty can, M1 (g)	1.0143
Mass of can + moist soil, M2 (g)	10.0501
Mass of can + dry soil, M3 (g)	6.9364
Mass of soil (g), M3-M1	5.9221
Pore Water mass (g), M2-M3	3.1137
Moisture content, w% = ((M2-M3)/(M3-M1))*100	52.6%
Number of blows, N	25
Plastic Limit Determination	
Mass of empty can, M1 (g)	1.0029
Mass of can + moist soil, M2 (g)	7.7962
Mass of can + dry soil, M3 (g)	6.7578
Mass of soil (g), M3-M1	5.7549
Pore Water mass (g), M2-M3	1.0384
Moisture content, w% = ((M2-M3)/(M3-M1))*100	18.04%

Therefore for soil S1, liquid limit (LL) = 52.6, plastic limit (PL) = 18.04 and plasticity index (PI) = LL – PL = 52.6 – 18.04 = 34.56.

According to the calculations shown in Table 4-1, the soil retained in No. 200 sieve (R_{200}) = 41.67%. Since $R_{200} \leq 50\%$, it is fine-grained soil. The group symbol for S1 soil was determined from Figure 4-3.
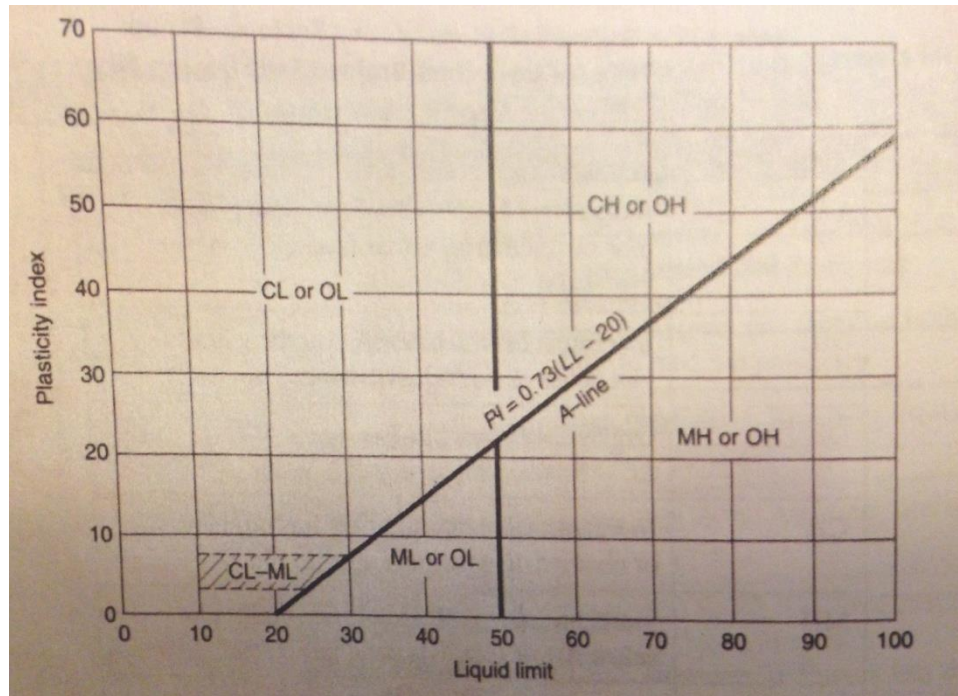
Figure 4-3 Plasticity chart for group symbols of fine-grained soils as per USCS

According to Figure 4-3, for S1 soil with LL = 52.6 and PI = 34.56, the group symbol therefore is CH – Inorganic clays of high plasticity, fat clays.

The liquid and plastic limit calculations for soil S2 are shown in Table 4-4.

Table 4-4 LL and PL calculation for soil S2

Liquid Limit Determination	
Mass of empty can, M1 (g)	0.9816
Mass of can + moist soil, M2 (g)	10.4066
Mass of can + dry soil, M3 (g)	8.1055
Mass of soil (g), M3-M1	7.1239
Pore Water mass (g), M2-M3	2.3011
Moisture content, w% = ((M2-M3)/(M3-M1))*100	32.30%
Number of blows, N	25
Plastic Limit Determination	
Mass of empty can, M1 (g)	1.031
Mass of can + moist soil, M2 (g)	7.4766
Mass of can + dry soil, M3 (g)	6.749
Mass of soil (g), M3-M1	5.718
Pore Water mass (g), M2-M3	0.7276
Moisture content, w% = ((M2-M3)/(M3-M1))*100	12.72%

Therefore for soil S2, the plastic limit (PI) = LL – PL = 32.30 – 12.72 = 19.58.

For S2 soil, according to the calculations shown in Table 4-2, the soil retained in No. 200 sieve (R_{200}) = 81.08%. Since $R_{200} \geq 50\%$, it is coarse-grained soil. For coarse-grained soils, the percent retained on No.4 U.S. sieve (R_4) = 100 – F_4 where F_4 is percent finer than No.4 sieve. From Table 4-2, F_4 = 98.65%. Therefore, R_4 = 100 – 98.65 = 1.35%. Now, $0.5 \cdot R_{200}$ = 40.54% which is less than R_4. Thus, it is sandy soil. The PI = 19.58 which is greater than 7. Therefore, the group symbol for S2 soil is SC (Soil Mechanics Laboratory Manual, 2009).

The preliminary tests are summarized in Table 4-5.

Table 4-5 Summary of preliminary tests of soils

Soil	LL	PL	PI	Type of soil	Group Symbol
S1	52.6	18.04	34.56	fine-grained	CH
S2	32.30	12.72	19.58	coarse-grained, sandy soil	SC

4.2 Column experiment results

The vertical distribution of methane was analyzed to derive the extent of methane removal in all the eight columns. Methane removal efficiency was calculated as given in Equation (4.1):

Methane removal efficiency =

$$\left(\frac{\text{methane\% measured from port 1} - \text{methane\% from port 3}}{\text{methane\% measured from port 1}}\right) * 100 \qquad \textbf{(4.1)}$$

The data collected for about a month from all columns is attached in the Appendix. A sample data for column 1 is provided in Table 4-6.

Table 4-6 Results for column 1

Day	CH$_4$ from bottom port (%)	CH4 from top port (%)	Mass in µg/min	Mass out µg/min	Mass Removal Rate, µg/min	Volumetric Mass Loading, g/min/m^3	Mass Removal Rate per Vol., g/min/m^3	Methane Removal Efficiency (%)
1	36.8	17.4	26269	12421	13848	1.245	0.66	53
2	10.6	1.5	7567	1071	6496	0.359	0.31	86
3	22.1	1.8	15775	1285	14491	0.748	0.69	92
4	34.5	9.7	24627	6924	17703	1.167	0.84	72
5	18.2	6.7	12992	4783	8209	0.616	0.39	63
6	13.2	3.2	9422	2284	7138	0.447	0.34	76
7	13.2	2.5	9422	1785	7638	0.447	0.36	81
8	20	7.5	14276	5354	8923	0.677	0.42	63
9	20.9	7.5	14919	5354	9565	0.707	0.45	64
10	26.8	19.1	19130	13634	5496	0.907	0.26	29
11	23.9	18.8	17060	13420	3640	0.809	0.17	21
12	30.9	23.2	22057	16561	5496	1.045	0.26	25
13	30.5	22.9	21772	16347	5425	1.032	0.26	25
14	30.9	22.5	22057	16061	5996	1.045	0.28	27
15	28.6	20	20415	14276	6139	0.968	0.29	30
16	15.9	11.7	11350	8352	2998	0.538	0.14	26
17	13.2	8	9422	5711	3712	0.447	0.18	39
18	26.4	19.1	18845	13634	5211	0.893	0.25	28
19	27.3	19.7	19487	14062	5425	0.924	0.26	28
20	29.5	21.8	21058	15561	5496	0.998	0.26	26
21	27.8	19.6	19844	13991	5853	0.940	0.28	29
22	23.6	17.9	16846	12777	4069	0.798	0.19	24
23	22.9	16.2	16347	11564	4783	0.775	0.23	29
24	22.1	16.2	15775	11564	4212	0.748	0.20	27
25	20	11.5	14276	8209	6067	0.677	0.29	43
26	24.6	16.2	17560	11564	5996	0.832	0.28	34
27	19.4	14.7	13848	10493	3355	0.656	0.16	24
28	27.3	19.4	19487	13848	5639	0.924	0.27	29
29	25.5	17.6	18202	12563	5639	0.863	0.27	31
30	18.2	11.8	12992	8423	4568	0.616	0.22	35
31	16.5	10.6	11778	7567	4212	0.558	0.20	36

The values in Table 4-6 have been calculated as follows:

Mass into column, µg/min has been calculated using Equation (4.2):

$$\text{Mass} = Q \text{ (flow rate) } * C \text{ (concentration, µg/L)} \qquad \textbf{(4.2)}$$

CH_4 from bottom port is the concentration in percentage. This value is converted into concentration in parts per million (C_{ppm}). Thus, $C_{ppm} = C (\%) * 10^4$ and:

$$\text{Mass in, µg/min} = \left(\frac{1000 * C_{ppm} \text{ in } * \text{Molecular weight}}{(\frac{RT}{P})} \right) * 80 \text{ ml/min} * (10^{-6}) \qquad \textbf{(4.3)}$$

where molecular weight of methane is 16 g/mole. R is ideal gas law constant = 0.08206 atm-L/gmol-K. Temperature is 22^0C or 295 K. Pressure is the average pressure at top and bottom of the column = (1+1.701atm)/2 = 1.35 atm.

Similarly mass out, µg/min, was calculated using Equation (4.4),

$$\text{Mass out µg/min} = \left(\frac{1000 * C_{ppm} \text{ out } * Molecular\ weight}{(\frac{RT}{P})} \right) * 80 \text{ ml/min} * (10^{-6}) \qquad \textbf{(4.4)}$$

Mass Removal Rate, µg/min = Mass in – Mass out

Volumetric Mass Loading, $g/min/m^3$ = (Mass in $*10^{-6}$)/volume of media,

where volume of media = $0.0211\ m^3$ for columns 1 to 6 and $0.0105\ m^3$ for columns 7 and 8. Diameter of column = 8.25 inches and length of media is 24 inches for columns 1 to 6 and; 12 inches for columns 7 and 8..

Mass Removal Rate per Volume, $g/min/m^3$ = (Mass Removal Rate, µg/min $*10^{-6}$) / 0.0211

Figures 4-4 to 4-11 show the elimination capacity (mass removal rate) vs. volumetric mass loading graphs for columns 1 to 8.
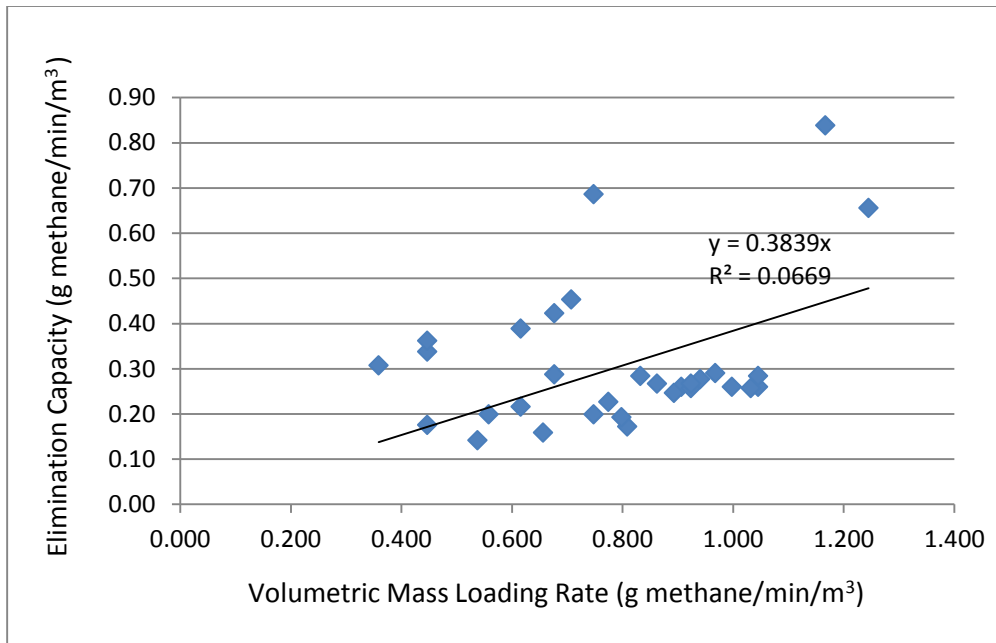
Figure 4-4 Elimination capacity vs. Volumetric mass loading rate for column 1 (S1)
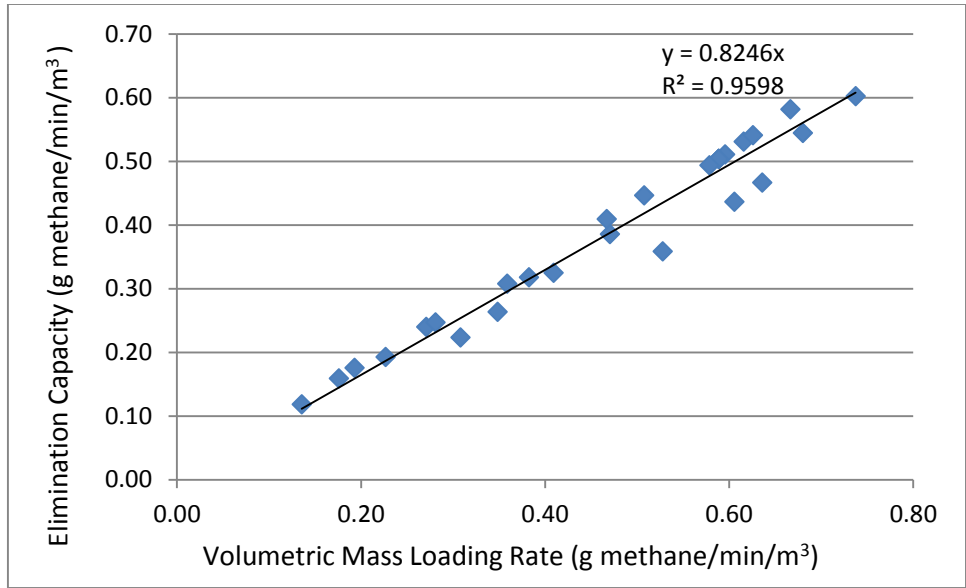
Figure 4-5 Elimination capacity vs. Volumetric mass loading rate for column 2 (S2)
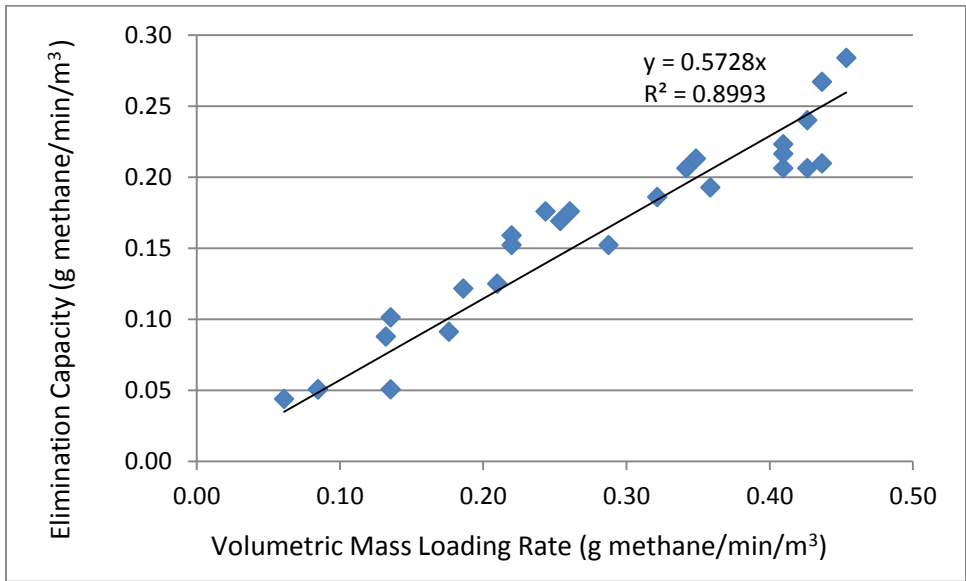
Figure 4-6 Elimination capacity vs. Volumetric mass loading rate for column 3 (70% S2, 30% F1)
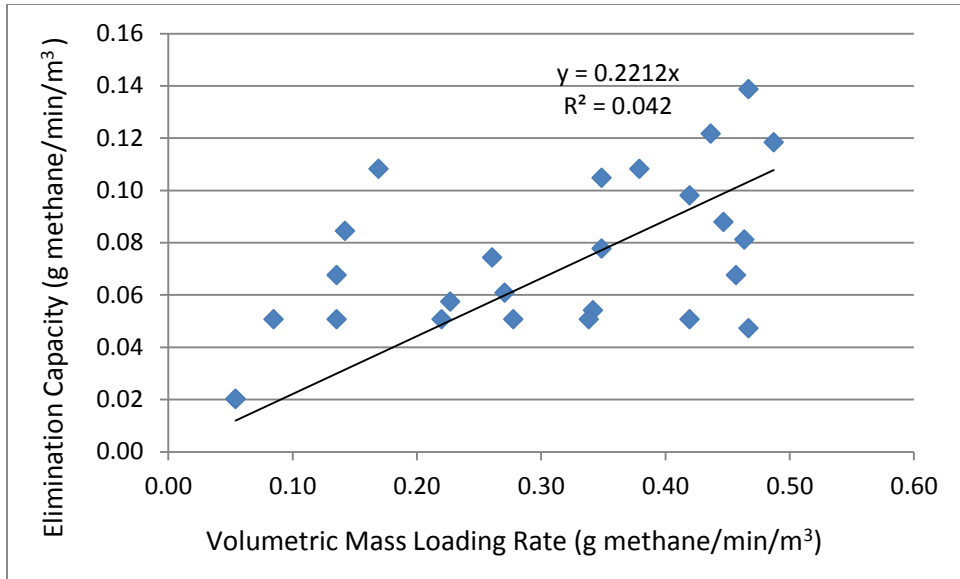
Figure 4-7 Elimination capacity vs. Volumetric mass loading rate for column 4 (70% S1, 30% F1)
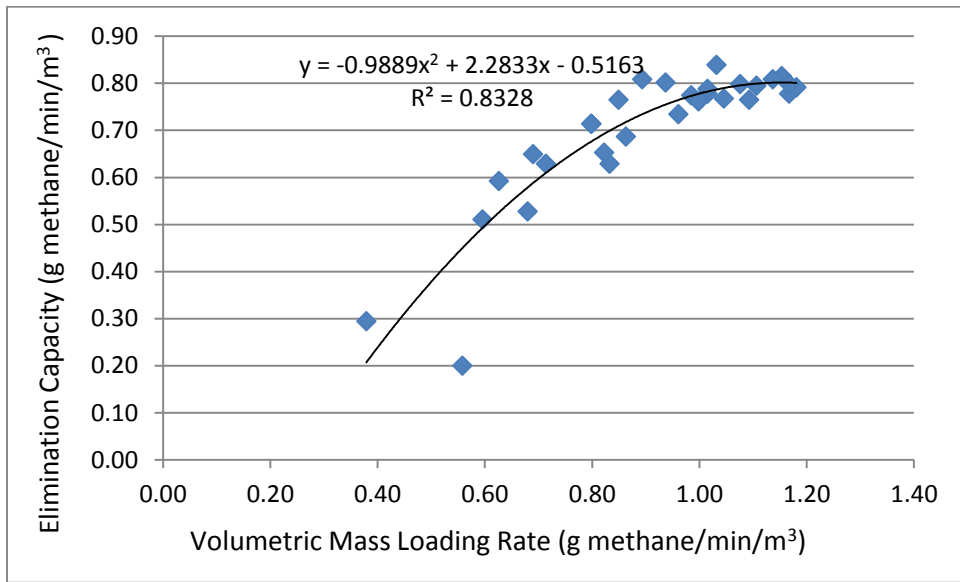
Figure 4-8 Elimination capacity vs. Volumetric mass loading rate for column 5 (70% S1, 30% F2)
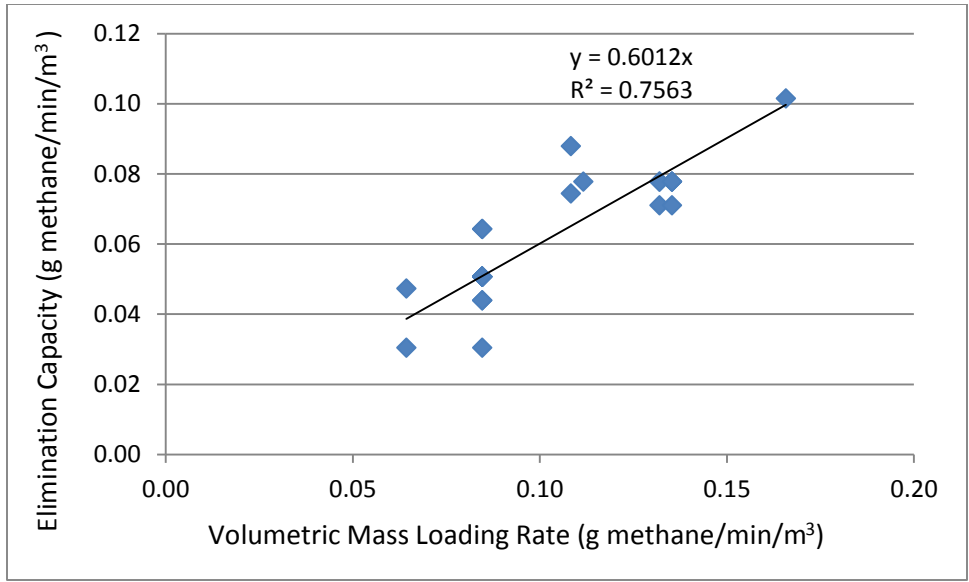
Figure 4-9 Elimination capacity vs. Volumetric mass loading rate for column 6 (70% S2, 30% F2)
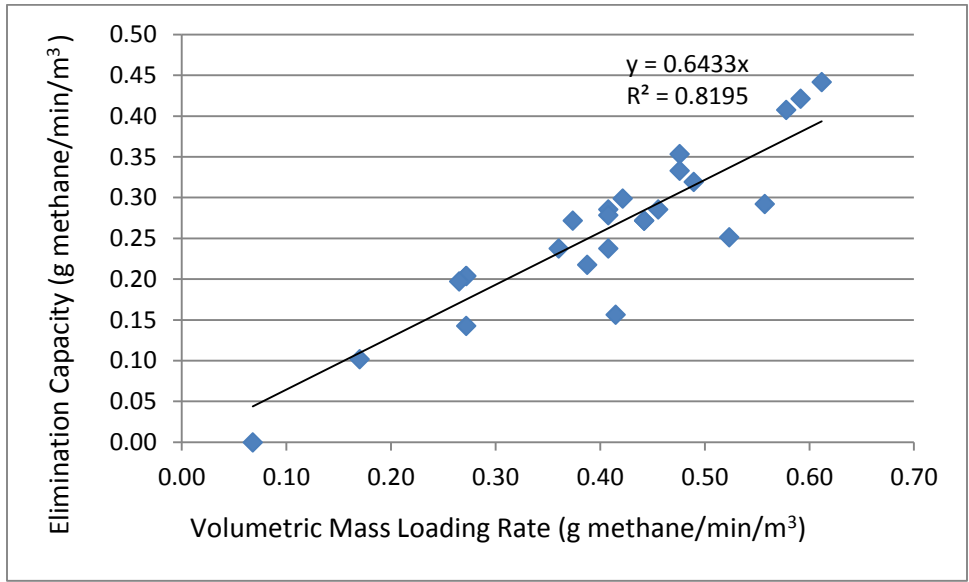
Figure 4-10 Elimination capacity vs. Volumetric mass loading rate for column 7 (F2)
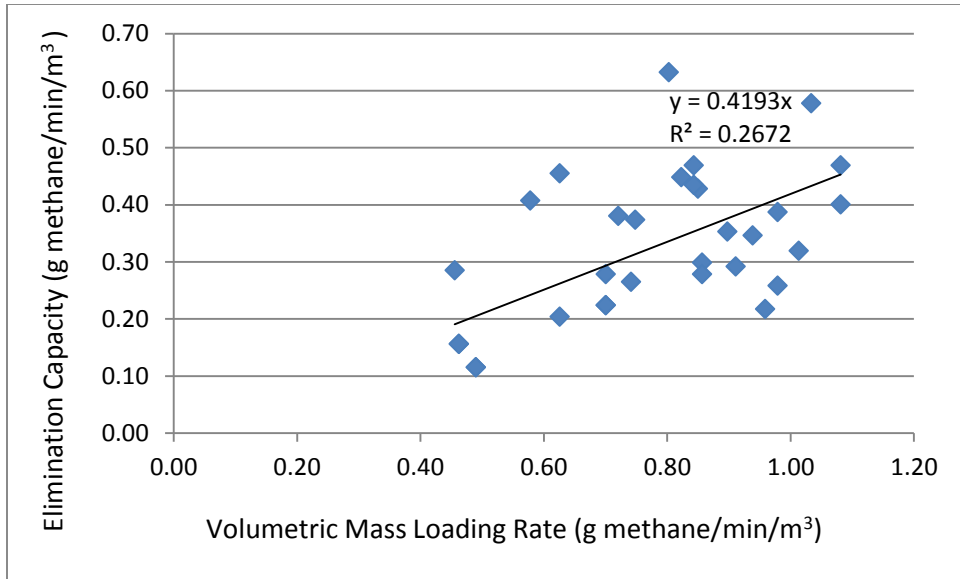
Figure 4-11 Elimination capacity vs. Volumetric mass loading rate for column 8 (F1)

Table 4-7 Summary of R^2 values from elimination capacity vs. mass loading curves

Column No.	Cover Composition		R^2 values from elimination capacity vs. mass loading curves
	Soil	Fly Ash	
1	S1 100%	0%	0.07
2	S2 100%	0%	0.96
3	S2 70%	F1 30%	0.90
4	S1 70%	F1 30%	0.04
5	S1 70%	F2 30%	0.83
6	S2 70%	F2 30%	0.76
7	0%	F2 100%	0.82
8	0%	F1 100%	0.27

Soil S2 has the higher R^2 values. The reason for this is unclear. The only graph that seems to have reached an asymptote is column 5 (S1 70% and F2 30%). If methane

oxidation by microbes is the mechanism, then the microbes had reached the maximum amount they could degrade. Else if, adsorption is the mechanism, then the adsorption sites were full. For the other columns, the maximum degradation or adsorption amount had not reached yet.

Samples of the two types of fly ash were given to the Department of Material Science and Engineering for X-ray photoelectron spectroscopy (XPS, Perkin-Elmer Phi 560 XPS/Auger System) and energy-dispersive X-ray spectroscopy (EDS, HitachiS-3000 N integrated with EDS) for determination of fly ash composition. Table 4-8 shows the fly ash composition of F1 and F2. The fly ashes contain 3-4% iron according to EDS, and 3-5% sulfur according to XPS, which could facilitate anaerobic methane oxidation. The presence of Si and Ti content according to XPS and EDS could also facilitate anaerobic methane oxidation. They also contain a high percent of carbon (40-55%), which could enable them to serve as an adsorbent.

Table 4-8 Fly ash composition

	XPS		EDS	
Element	F1	F2	F1	F2
O	46.36	41.17	33.61	30.27
C	39.64	45.44	47.41	55.24
Na	2.19	0	0.62	0.26
Ca	0	0.18	0.54	0.24
S	5.01	3.65	0.37	0.23
Si	5.43	4.79	7.88	5.91
Al	0.91	4.02	4.13	3.66
Mg	0	0	0.10	0.16
Zn	0.44	0.74	0	0
Fe	0	0	4.19	2.96
K	0	0	0.79	0.81
Ti	0	0	0.36	0.27
TOTAL	99.98	99.99	100.00	100.00

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition at the parts per thousand range, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the material being analyzed (X-ray photoelectron spectroscopy – Wikipedia).

EDS is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray emission spectrum. The differences in percentages for the composition of elements in XPS and EDS analysis given in Table 4-8 are mainly because XPS analysis is much more surface-limited than EDS.

Table 4-9 shows average methane removal percentage for the soils, fly ashes, and soil/fly ash combinations tested. Soils S1 (high plasticity clay) and S2 (clayey sand), tested alone in columns 1 and 2, achieved 42% and 83% removal efficiencies respectively for methane. This could be due to anaerobic oxidation of methane by soil microbes, or adsorption of methane onto soil. Fly Ashes 1 and 2 tested alone in columns 8 and 7, achieved removal efficiencies of 43% and 62%, respectively. Since fly ash alone would not be anticipated to contain microbes, this is likely due to adsorption.

Thus, four mechanisms may be involved in methane removal namely, methane oxidation by microbes, adsorption, absorption and chemical oxidation by fly ash.

Table 4-9 Simulated landfill cover compositions and removal efficiencies at flow rate of 80 ml/min

Column No.	Cover Composition		Average Methane Removal Efficiency (%)
	Soil	Fly Ash	
1	S1 100%	0%	42%
2	S2 100%	0%	83%
3	S2 70%	F1 30%	60%
4	S1 70%	F1 30%	29%
5	S1 70%	F2 30%	78%
6	S2 70%	F2 30%	60%
7	0%	F2 100%	62%
8	0%	F1 100%	43%

Fly Ash 1 in column 4 did not increase the removal efficiency over soil alone in column 1. However, Fly Ash 2 substantially increased methane removal efficiency in Column 5. Fly Ash 1 may not have increased the removal efficiency of Soil 2 in column 3, because its removal efficiency was already high.

In order to determine if the fly ash makes any difference at a higher methane feed rate, the flow rate was increased from 80 ml/min to 120 ml/min for columns containing soil S2; that is, columns 2, 3 and 6. Table 4-10 shows average methane removal percentage for columns 2, 3 and 6 at 80 ml/min and 120 ml/min.

Table 4-10 Comparison between removal efficiencies at flow rates 80 and 120 ml/min

Column No.	Cover Composition		Average Methane Removal Efficiency (%) at 80 ml/min	Average Methane Removal Efficiency (%) at 120 ml/min
	Soil	Fly Ash		
2	S2 100%	0%	83%	58%
3	S2 70%	F1 30%	60%	46%
6	S2 70%	F2 30%	60%	66%

After increasing the flow rate to 120 ml/min, columns 2, 3, and 6, which contain Soil 2, showed removal efficiencies of 58%, 46%, and 66% respectively. For column 2, the removal efficiency dropped from 83% to 58% at the higher methane mass flow rate. This indicates that the soil by itself was no longer able to remove as much methane, via either biodegradation or adsorption. For column 3 with 30% fly ash F1, the removal percent is 60% vs. 46%. This indicates that at higher flow rate, the fly ash F1 is decreasing removal efficiency in column 3. For column 6 with 30% fly ash F2, the removal percent is 60% vs. 66% (lower flow rate vs. higher flow rate). This indicates that fly ash F2 is improving methane removal at higher flow rate.

It is somewhat surprising that fly ash F2 is increasing methane removal more than F1, given that percents of elements likely to facilitate anaerobic biological methane oxidation (Fe, S, Si, and Ti) were higher for fly ash 1. However, we see that fly ash F2 has higher percent of carbon. This may indicate that the methane removal mechanism is adsorption.

Biological decomposition of methane occurs in two steps – absorption of methane into the liquid phase and then biological oxidation. Therefore it is imperative for absorption to occur in a time shorter than the empty bed residence time (EBRT) i.e. time

a parcel of gas will remain in an empty biofilter. Similarly, adsorption too needs to occur in a time less than EBRT. Table 4-11 shows the empty bed residence time (EBRT) in the columns.

Table 4-11 Empty bed residence time (EBRT) in columns

Column	Volume of media, m^3 (V)	Flow rate, mL/min (Q)	EBRT, V/Q (hours)
1 to 6	0.021	80	4.4
7 & 8	0.0105	80	2.2

This means that both absorption of methane into water film and adsorption must occur in less than 4.4 hours in columns 1 to 6; and 2.2 hours in columns 7 and 8.

4.3 Moisture content

Due to the gas leak at the moisture ports after 2 weeks, the ports were sealed. 2 weeks of moisture data therefore could only be taken. Although constant moisture was supplied with the help of the humidifiers, the moisture content of the soil and/fly ash mixtures from all the eight columns was calculated at the end of the experiment as a precaution. Three samples of soil and/fly ash mixture were taken from each of the eight columns from the upper, middle and lower layers of the columns to get a representative value. Table 4-11 shows the average moisture content in all the columns calculated at the end of the experiment. The average moisture content in all the columns ranged from 10% to 14%, which was within the range of optimum moisture content of 10% to 20% required to maintain a balanced environment in the cover soil for CH_4 oxidation (Chanton et al., 2011a, b; Spokas and Bogner 2011).

Table 4-12 Average moisture content of soil and/ fly ash mixtures in columns

Column	Average moisture content (%)
1	13.7
2	12.6
3	11
4	11.4
5	12.1
6	12.6
7	9.8
8	10.5

Chapter 5

Conclusions and Recommendations

The main objective of this research was to determine which combination of soil and fly ash work best in enhancing the methane removal in landfill cover. Fly ash 2 increased methane removal for soil 1. This combination worked best in enhancing methane removal. Fly ash 1 did not substantially increase methane removal for either kind of soil. This is surprising, given that percents of elements likely to facilitate anaerobic biological methane oxidation (Fe, S, Si, and Ti) were higher for fly ash 1. These may indicate that the methane removal mechanism is adsorption. Also, higher percent of carbon in fly ash 2 may have aided removal via adsorption. Fly ash 2 removed 62% methane by itself, compared to 43% for fly ash 1. This further indicates that the removal mechanism is likely adsorption, because fly ash by itself should not contain any microbes to facilitate oxidation.

On the basis of the experimental results and problems faced during the project, the following are the general recommendations made for future study.

- Characterize fly ash in terms of surface chemistry, mineralogy and reactivity in order to understand better the mechanism involved in methane removal.
- Use the soil/fly ash combination from this study that produces the highest methane oxidation and run duplicates.
- Heat the soil to high temperatures to inactivate the microbes, to be able to distinguish biological removal from adsorption.
- Increase mass loading rates to find asymptote for elimination capacity.
- Test with 100% CO_2 as a check, measuring inlet and outlet concentrations (which should be the same).

- Determine optimum ratio of soil/fly ash.

- Test conditions more similar to real landfill cover- compacted soil and oxygen present in upper layers of soil.

- Measure kinetics of removal (how fast removal occurs).

- Examine impact of varying moisture content, as well as methane/oxygen ratio at the top of the cover (simulating actual landfill conditions).

- Measure surface areas of the fly ash (higher surface area may increase adsorption).

- Better understanding of methanotrophic activity.

The following are the recommendations pertaining to improving the experimental set up.

- Measure methane concentration at column inlet. Although 50% methane is passed into the column, the bottom port for most columns read 30% to 40%. Measuring the methane concentration at column inlet will help us know where exactly the gas loss is. Appropriate actions can thereafter be taken.

- Humidification
    - Add fish tank frit to the bottom of the tube to break bubbles into smaller bubbles to avoid large bubbles causing fluctuations in concentrations.
    - Install humidity sensors to prevent gas leaks and obtain reliable moisture data.
    - Install ports to measure methane before and after humidifiers.

- Address potential leaks:
    - Measure oxygen levels in reactor.
    - Seal and clamp the experimental set up to make it gas tight.

> ➢ Measure methane using gas chromatograph. Using an auto-injector to
> do so will give consistent data.

- Insert needle tubes in columns instead of using methane sensor for reliable data.

Appendix A

Column Results

Results for column 2 containing 100% soil 2

Day	CH$_4$ from bottom port (%)	CH4 from top port (%)	Mass in µg/min	Mass out µg/min	Mass Removal Rate, µg/min	Volumetric Mass Loading, g/min/m^3	Mass Removal Rate per Vol., g/min/m^3	Methane Removal Efficiency (%)
1	4	0.5	2855	357	2498	0.14	0.12	88
2	5.7	0.5	4069	357	3712	0.19	0.18	91
3	5.2	0.5	3712	357	3355	0.18	0.16	90
4	8	0.9	5711	642	5068	0.27	0.24	89
5	8.3	1	5925	714	5211	0.28	0.25	88
6	13.9	2.5	9922	1785	8138	0.47	0.39	82
7	10.3	2.5	7352	1785	5568	0.35	0.26	76
8	21.8	4	15561	2855	12706	0.74	0.60	82
9	15.6	5	11136	3569	7567	0.53	0.36	68
10	18.8	5	13420	3569	9851	0.64	0.47	73
11	17.9	5	12777	3569	9208	0.61	0.44	72
12	9.1	2.5	6496	1785	4711	0.31	0.22	73
13	6.7	1	4783	714	4069	0.23	0.19	85
14	17.4	2.5	12421	1785	10636	0.59	0.50	86
15	17.4	2.5	12421	1785	10636	0.59	0.50	86
16	19.7	2.5	14062	1785	12278	0.67	0.58	87
17	17.6	2.5	12563	1785	10779	0.60	0.51	86
18	12.1	2.5	8637	1785	6853	0.41	0.32	79
19	11.3	1.9	8066	1356	6710	0.38	0.32	83
20	17.4	2.5	12421	1785	10636	0.59	0.50	86
21	10.6	1.5	7567	1071	6496	0.36	0.31	86
22	18.2	2.5	12992	1785	11207	0.62	0.53	86
23	17.1	2.5	12206	1785	10422	0.58	0.49	85
24	20.1	4	14348	2855	11493	0.68	0.54	80
25	18.5	2.5	13206	1785	11421	0.63	0.54	86
26	13.8	1.7	9851	1213	8637	0.47	0.41	88
27	15	1.8	10707	1285	9422	0.51	0.45	88

Results for column 3 containing 30% fly ash 1 and soil 2

Day	CH$_4$ from bottom port (%)	CH4 from top port (%)	Mass in µg/min	Mass out µg/min	Mass Removal Rate, µg/min	Volumetric Mass Loading, g/min/m^3	Mass Removal Rate per Vol., g/min/m^3	Methane Removal Efficiency (%)
1	1.8	0.5	1285	357	928	0.06	0.04	72.22
2	2.5	1	1785	714	1071	0.08	0.05	60.00
3	2.5	1	1785	714	1071	0.08	0.05	60.00
4	6.5	1.8	4640	1285	3355	0.22	0.16	72.31
5	6.5	2	4640	1428	3212	0.22	0.15	69.23
6	13.4	5	9565	3569	5996	0.45	0.28	62.69
7	12.9	5	9208	3569	5639	0.44	0.27	61.24
8	12.1	5.5	8637	3926	4711	0.41	0.22	54.55
9	12.1	6	8637	4283	4354	0.41	0.21	50.41
10	12.6	6.5	8994	4640	4354	0.43	0.21	48.41
11	12.9	6.7	9208	4783	4426	0.44	0.21	48.06
12	7.2	2	5140	1428	3712	0.24	0.18	72.22
13	4	1	2855	714	2141	0.14	0.10	75.00
14	9.5	4	6781	2855	3926	0.32	0.19	57.89
15	10.6	4.9	7567	3498	4069	0.36	0.19	53.77
16	12.6	5.5	8994	3926	5068	0.43	0.24	56.35
17	10.1	4	7210	2855	4354	0.34	0.21	60.40
18	8.5	4	6067	2855	3212	0.29	0.15	52.94
19	7.5	2.5	5354	1785	3569	0.25	0.17	66.67
20	7.7	2.5	5496	1785	3712	0.26	0.18	67.53
21	3.9	1.3	2784	928	1856	0.13	0.09	66.67
22	5.5	1.9	3926	1356	2570	0.19	0.12	65.45
23	4	2.5	2855	1785	1071	0.14	0.05	37.50
24	12.1	5.7	8637	4069	4568	0.41	0.22	52.89
25	10.3	4	7352	2855	4497	0.35	0.21	61.17
26	5.2	2.5	3712	1785	1927	0.18	0.09	51.92
27	6.2	2.5	4426	1785	2641	0.21	0.13	59.68

Results for column 4 containing 30% fly ash 1 and soil 1

Day	CH$_4$ from bottom port (%)	CH4 from top port (%)	Mass in μg/min	Mass out μg/min	Mass Removal Rate, μg/min	Volumetric Mass Loading, g/min/m^3	Mass Removal Rate per Vol., g/min/m^3	Methane Removal Efficiency (%)
1	1.6	1	1142.1	713.8	428.3	0.05	0.02	38
2	1.6	1	1142.1	713.8	428.3	0.05	0.02	38
3	4	2.5	2855.3	1784.6	1070.7	0.14	0.05	38
4	4	2	2855.3	1427.6	1427.6	0.14	0.07	50
5	10.1	8.5	7209.6	6067.5	1142.1	0.34	0.05	16
6	7.7	5.5	5496.4	3926.0	1570.4	0.26	0.07	29
7	13.2	10.6	9422.5	7566.5	1855.9	0.45	0.09	20
8	12.4	10.9	8851.4	7780.7	1070.7	0.42	0.05	12
9	13.5	11.5	9636.6	8209.0	1427.6	0.46	0.07	15
10	13.7	11.3	9779.4	8066.2	1713.2	0.46	0.08	18
11	4.2	1.7	2998.1	1213.5	1784.6	0.14	0.08	60
12	5	1.8	3569.1	1284.9	2284.2	0.17	0.11	64
13	10.3	8	7352.4	5710.6	1641.8	0.35	0.08	22
14	12.4	9.5	8851.4	6781.3	2070.1	0.42	0.10	23
15	14.4	10.9	10279.0	7780.7	2498.4	0.49	0.12	24
16	12.9	9.3	9208.3	6638.5	2569.8	0.44	0.12	28
17	11.2	8	7994.8	5710.6	2284.2	0.38	0.11	29
18	8.2	6.7	5853.3	4782.6	1070.7	0.28	0.05	18
19	10	8.5	7138.2	6067.5	1070.7	0.34	0.05	15
20	6.7	5	4782.6	3569.1	1213.5	0.23	0.06	25
21	10.3	7.2	7352.4	5139.5	2212.8	0.35	0.10	30
22	2.5	1	1784.6	713.8	1070.7	0.08	0.05	60
23	13.8	12.4	9850.7	8851.4	999.4	0.47	0.05	10
24	13.8	9.7	9850.7	6924.1	2926.7	0.47	0.14	30
25	8	6.2	5710.6	4425.7	1284.9	0.27	0.06	23
26	6.5	5	4639.8	3569.1	1070.7	0.22	0.05	23

Results for column 5 containing 30% fly ash 2 and soil 1

Day	CH$_4$ from bottom port (%)	CH4 from top port (%)	Mass in µg/min	Mass out µg/min	Mass Removal Rate, µg/min	Volumetric Mass Loading, g/min/m^3	Mass Removal Rate per Vol., g/min/m^3	Methane Removal Efficiency (%)
1	11.2	2.5	7995	1785	6210	0.38	0.29	78
2	21.1	2.5	15062	1785	13277	0.71	0.63	88
3	23.6	2.5	16846	1785	15062	0.80	0.71	89
4	26.4	2.5	18845	1785	17060	0.89	0.81	91
5	18.5	1	13206	714	12492	0.63	0.59	95
6	20.4	1.2	14562	857	13705	0.69	0.65	94
7	23.6	2.5	16846	1785	15062	0.80	0.71	89
8	25.1	2.5	17917	1785	16132	0.85	0.76	90
9	28.4	6.7	20273	4783	15490	0.96	0.73	76
10	24.6	6	17560	4283	13277	0.83	0.63	76
11	32.3	9.7	23056	6924	16132	1.09	0.76	70
12	34.1	10	24341	7138	17203	1.15	0.82	71
13	34.5	11.5	24627	8209	16418	1.17	0.78	67
14	34.9	11.5	24912	8209	16703	1.18	0.79	67
15	20.1	4.5	14348	3212	11136	0.68	0.53	78
16	17.6	2.5	12563	1785	10779	0.60	0.51	86
17	30	7	21415	4997	16418	1.01	0.78	77
18	31.8	8.2	22700	5853	16846	1.08	0.80	74
19	33.6	9.7	23984	6924	17060	1.14	0.81	71
20	30.9	8.2	22057	5853	16204	1.05	0.77	73
21	29.1	6.2	20772	4426	16347	0.98	0.77	79
22	30.5	5.7	21772	4069	17703	1.03	0.84	81
23	29.5	7	21058	4997	16061	1.00	0.76	76
24	27.7	4	19773	2855	16918	0.94	0.80	86
25	30	6.7	21415	4783	16632	1.01	0.79	78
26	24.3	5	17346	3569	13777	0.82	0.65	79
27	34.5	10.9	24627	7781	16846	1.17	0.80	68
28	32.7	9.2	23342	6567	16775	1.11	0.80	72
29	25.5	5.2	18202	3712	14491	0.86	0.69	80
30	16.5	10.6	11778	7567	4212	0.56	0.20	36

Results for column 6 containing 30% fly ash 2 and soil 2

Day	CH$_4$ from bottom port (%)	CH4 from top port (%)	Mass in µg/min	Mass out µg/min	Mass Removal Rate, µg/min	Volumetric Mass Loading, g/min/m^3	Mass Removal Rate per Vol., g/min/m^3	Methane Removal Efficiency (%)
1	1.9	0.5	1356	357	999	0.06	0.05	74
2	2.5	0.6	1785	428	1356	0.08	0.06	76
3	2.5	1	1785	714	1071	0.08	0.05	60
4	3.2	1	2284	714	1570	0.11	0.07	69
5	3.3	1	2356	714	1642	0.11	0.08	70
6	3.9	1.6	2784	1142	1642	0.13	0.08	59
7	2.5	1	1785	714	1071	0.08	0.05	60
8	4	1.7	2855	1213	1642	0.14	0.08	58
9	4.9	1.9	3498	1356	2141	0.17	0.10	61
10	3.9	1.8	2784	1285	1499	0.13	0.07	54
11	4	1.7	2855	1213	1642	0.14	0.08	58
12	3.2	0.6	2284	428	1856	0.11	0.09	81
13	2.5	0.6	1785	428	1356	0.08	0.06	76
14	2.5	1	1785	714	1071	0.08	0.05	60
15	2.5	1.2	1785	857	928	0.08	0.04	52
16	3.9	1.6	2784	1142	1642	0.13	0.08	59
17	2.5	1.6	1785	1142	642	0.08	0.03	36
18	2.5	1.2	1785	857	928	0.08	0.04	52
19	2.5	1	1785	714	1071	0.08	0.05	60
20	2.5	1	1785	714	1071	0.08	0.05	60
21	2.5	1	1785	714	1071	0.08	0.05	60
22	2.5	1	1785	714	1071	0.08	0.05	60
23	2.5	1	1785	714	1071	0.08	0.05	60
24	4	1.9	2855	1356	1499	0.14	0.07	53
25	4	1.7	2855	1213	1642	0.14	0.08	58
26	1.9	1	1356	714	642	0.06	0.03	47
27	2.5	1	1785	714	1071	0.08	0.05	60

Results for column 7 containing fly ash 1 only

Day	CH$_4$ from bottom port (%)	CH4 from top port (%)	Mass in µg/min	Mass out µg/min	Mass Removal Rate, µg/min	Volumetric Mass Loading, g/min/m^3	Mass Removal Rate per Vol., g/min/m^3	Methane Removal Efficiency (%)
1	4	1	2855	714	2141	0.27	0.20	75
2	2.5	1	1785	714	1071	0.17	0.10	60
3	4	1	2855	714	2141	0.27	0.20	75
4	1	1	714	714	0	0.07	0.00	0
5	7	1.8	4997	1285	3712	0.48	0.35	74
6	7	2.1	4997	1499	3498	0.48	0.33	70
7	6.7	2.5	4783	1785	2998	0.46	0.29	63
8	6.2	1.8	4426	1285	3141	0.42	0.30	71
9	8.7	2.5	6210	1785	4426	0.59	0.42	71
10	9	2.5	6424	1785	4640	0.61	0.44	72
11	7.7	4	5496	2855	2641	0.52	0.25	48
12	6.1	3.8	4354	2713	1642	0.41	0.16	38
13	5.3	1.8	3783	1285	2498	0.36	0.24	66
14	3.9	1	2784	714	2070	0.27	0.20	74
15	5.5	1.5	3926	1071	2855	0.37	0.27	73
16	6	1.8	4283	1285	2998	0.41	0.29	70
17	6	2.5	4283	1785	2498	0.41	0.24	58
18	6.5	2.5	4640	1785	2855	0.44	0.27	62
19	5.7	2.5	4069	1785	2284	0.39	0.22	56
20	7.2	2.5	5140	1785	3355	0.49	0.32	65
21	6.5	2.5	4640	1785	2855	0.44	0.27	62
22	8.2	3.9	5853	2784	3069	0.56	0.29	52
23	8.5	2.5	6067	1785	4283	0.58	0.41	71
24	4	1.9	2855	1356	1499	0.27	0.14	53
25	6	1.9	4283	1356	2927	0.41	0.28	68

Results for column 8 containing fly ash 2 only

Day	CH$_4$ from bottom port (%)	CH4 from top port (%)	Mass in μg/min	Mass out μg/min	Mass Removal Rate, μg/min	Volumetric Mass Loading, g/min/m^3	Mass Removal Rate per Vol., g/min/m^3	Methane Removal Efficiency (%)
1	11.8	2.5	8423	1785	6639	0.80	0.63	79
2	6.7	2.5	4783	1785	2998	0.46	0.29	63
3	8.5	2.5	6067	1785	4283	0.58	0.41	71
4	10.6	5	7567	3569	3997	0.72	0.38	53
5	12.4	5.5	8851	3926	4925	0.84	0.47	56
6	12.1	5.5	8637	3926	4711	0.82	0.45	55
7	12.5	6.2	8923	4426	4497	0.85	0.43	50
8	12.4	6	8851	4283	4568	0.84	0.44	52
9	15.9	9	11350	6424	4925	1.08	0.47	43
10	15.9	10	11350	7138	4212	1.08	0.40	37
11	14.1	10.9	10065	7781	2284	0.96	0.22	23
12	13.4	9.1	9565	6496	3069	0.91	0.29	32
13	11	5.5	7852	3926	3926	0.75	0.37	50
14	9.2	2.5	6567	1785	4783	0.63	0.46	73
15	12.6	8.2	8994	5853	3141	0.86	0.30	35
16	13.2	8	9422	5711	3712	0.90	0.35	39
17	14.4	10.6	10279	7567	2713	0.98	0.26	26
18	14.9	10.2	10636	7281	3355	1.01	0.32	32
19	15.2	6.7	10850	4783	6067	1.03	0.58	56
20	14.4	8.7	10279	6210	4069	0.98	0.39	40
21	10.9	7	7781	4997	2784	0.74	0.27	36
22	10.3	7	7352	4997	2356	0.70	0.22	32
23	7.2	5.5	5140	3926	1213	0.49	0.12	24
24	6.8	4.5	4854	3212	1642	0.46	0.16	34
25	10.3	7	7352	4997	2356	0.70	0.22	32
26	7.2	5.5	5140	3926	1213	0.49	0.12	24
27	6.8	4.5	4854	3212	1642	0.46	0.16	34
28	10.3	6.2	7352	4426	2927	0.70	0.28	40
29	13.8	8.7	9851	6210	3640	0.94	0.35	37
30	9.2	6.2	6567	4426	2141	0.63	0.20	33
31	12.6	8.5	8994	6067	2927	0.86	0.28	33

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