FACTA UNIVERSITATIS
Series: **Working and Living Environmental Protection** Vol. 12, N° 3, 2015, pp. 329 - 339

GENERATION AND MONITORING OF METHANE AT A MUNICIPAL WASTE LANDFILL

UDC 628.473.2/.6

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Abstract. *This paper describes oxidation reactions of methane, as the prevalently emitted landfill gas, as well as reactions of oxidative pyrolysis with all the important factors influencing the final amount of methane emission: air temperature, landfill body temperature, pressure, humidity, and soil structure. Based on theoretical background and measures of methane emissions at 24 measuring points at the "Meteris" landfill in the town of Vranje, we analyzed the data on methane exceeding the maximum allowable values in ambient air and the possibility of a fire due to methane's flammability limit being reached. The paper also provides a description of the "Meteris" landfill general features.*

Key words: *waste, landfill, landfill gas, methane*

1. INTRODUCTION

The composition of landfill gas (LFG) emitted from a municipal solid waste landfill depends on waste composition, degradation phase, and the type of reactions occurring at a landfill at a given location at a given time. To a large extent, waste comprises easily biodegradable organic material and, as such, produces a substantial amount of LFG. LFG generation rate is proportional to waste degradation rate. LFG waste generation usually begins 200 days after the waste has been disposed of at the landfill.

A large landfill can generate LFG for a period over 50 years in the range from 0.06 to 0.53 [m^3/kg]. The calorific value of a typical LFG is ca. 16.8 [MJ/m^3] or approximately a half of the lower calorific value of natural gas [3].

As opposed to natural methane-generating environments, such as wetlands, landfills are potential sources, so it is necessary to know the amount and trends of methane generation in order to predict its role in climate changes. If one considers the causes of the greenhouse effect, 78% of the cases are due to CO_2, 8% due to CH_4, 9% due to N_2O, and 5% due to

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Received October 14, 2014 / Accepted February 5, 2016

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CFCs and SF_6 [12]. Methane is considered one of the most prominent greenhouse gases as its global warming potential has been estimated at more than 20 times higher than carbon dioxide and its atmospheric concentration increases by 1-2% annually.

2. LANDFILL GAS GENERATION

Methane and carbon dioxide are the prevalent LFG constituents. The chemical reaction for anaerobic biodegradation of solid organic waste into methane and carbon dioxide can be expressed as follows [10]:

$$C_aH_bO_c + \left(\frac{4a-b-2c}{4}\right)H_2O \rightarrow \left(\frac{4a+b-2c}{8}\right)CH_4 + \left(\frac{4a-b+2c}{8}\right)CO_2 \tag{1}$$

The decomposition of cellulose in the final volumetric composition of 50% methane and 50% carbon dioxide can be expressed with the chemical reaction

$$C_6H_{10}O_5 + H_2O \rightarrow 3CH_4 + 3CO_2 \tag{2}$$

The following is the chemical reaction for aerobic biodegradation of solid organic waste into carbon dioxide and water:

$$C_aH_bO_c + \left(\frac{4a+b-2c}{4}\right)O_2 \rightarrow aCO_2 + \frac{b}{2}H_2O \tag{3}$$

The following reaction represents the by-products obtained from aerobic degradation of one mole of cellulose:

$$C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O \tag{4}$$

Based on the percentage of nitrogen (79%vol) and oxygen (21%vol) in the air, it may be assumed that all the oxygen will not suffice to cause complete waste degradation, which will result in the presence of methane and carbon dioxide in the landfill body.

3. FACTORS INFLUENCING LANDFILL GAS GENERATION

The factors influencing LFG generation include type of waste, size of deposited material, height of deposited waste, pH value, temperature, and moisture content.

3.1. Type of waste

Waste can be organic or inorganic. Organic waste, such as food, garden waste, and paper, degrades faster than inorganic waste. Research indicates that yard waste contributes to methane generation up to 20%, while paper waste contributes from 30 to 50% [6].

Organic materials disposed of at a landfill are divided into two categories:

1. Fast-degrading materials (from three months to five years) and
2. Slow-degrading materials (up to 25 years).

The degradation rate usually reaches its maximum within the first two years and then gradually decreases. LFG generation begins near the end of the first year of a landfill's operation.

3.2. Size of deposited waste

LFG generation increases with the decrease in the contact surface area of waste. A smaller contact surface area has a larger absorption surface area of exposure to parameters such as water molecules, nutrient molecules, and bacteria.

3.3. Height of deposited waste

LFG generation increases with the increase in waste height. A projected height of waste 40 metres (or more) is the standard design of an LFG recovery facility [7].

3.4. pH value

Optimal pH values for anaerobic conditions range from 6.4 to 7.4. Landfill pH values might depend on the discharge of industrial wastes, alkalinity, and clean water infiltration [2]. When methane is being generated, the average pH value at the landfill does not fall below 6.2.

3.5. Temperature

Landfill temperature best indicates the type of bacteria active in anaerobic degradation. For instance, mesophilic bacteria, typical for the anaerobic phase during methane generation, multiply the fastest at 20 to 40°C, whereas thermophilic bacteria multiply the fastest at 45°C [8].

3.6. Moisture content

Methane generation rate increases with higher moisture content. In the majority of landfills, moisture is not equally distributed. When moisture content is low, the biogas generation curve is linear and it extends over a longer period of time. Maximum LFG generation requires an optimal moisture content of approximately 40 to 45% [7]. LFG generation can increase after heavy precipitation with high moisture content of 80%.

4. LANDFILL GAS MOVEMENT

LFG, generated inside the landfill body, can migrate through the soil or through the air (dispersion). LFG will migrate from the landfill along the path of least resistance due to pressure gradient, density, and concentration gradient. Methane is lighter than both air and carbon dioxide. LFG moves upwards through the landfill surface either into the gas recovery system or into ambient air. Highly porous materials such as fine sand and gravel will provide better passage for LFGs than dense compact soils such as arable land, silt, and clay. The upward LFG movement can be hindered by compacted waste or the landfill cover. This may result in horizontal LFG movement through the landfill body and into the surrounding land, piping, or other structures if there is no adequate LFG recovery system.

Saturated soils (wet soils) act as a barrier and interfere with the LFG flow through the soil. Gas emission into ambient air varies over time both daily and seasonally, and it depend on a number of factors, including the LFG generation rate, LFG composition, pressure gradients, gas control systems, terrain topography, and meteorological conditions.

LFG moves upwards and downwards through the landfill. During upward movement, methane and carbon dioxide are released into the atmosphere by means of two mechanisms: diffusion and convection.

Diffusion is spontaneous transport of a material influenced by specific concentration gradients from a higher-concentration to a lower-concentration zone. Diffusion is an entropy-guided process, in which the diffusing material is uniformly arranged within the available space until the system reaches the state of balance. Methane and carbon dioxide are lighter than the surrounding gases, so they will be emitted from the landfill body into the air.

Convection is the flow of fluids that occurs due to pressure gradients and the buoyant force, so it has an important role in LFG migration from the landfill body [11]. Darcy's law can be expressed via convective velocity through a vertical direction:

$$V_z = -\frac{k\ dp}{\mu\ dz} \tag{5}$$

where: V_z – convective velocity [m/s],
k – intrinsic permeability [m^2],
μ – gas mixture viscosity [Pa·s],
p – pressure [Pa],
z – depth [m].

If absorption and gas generation are taken into consideration, the LFG convection can be expressed as

$$O = V_z \frac{dC_a}{dz} + D_z \frac{d^2C_a}{dz^2} \tag{6}$$

where: O – LFG convection [g/m^{3}s],
C_a – compound concentration [g/m^3],
D_z – effective diffusion coefficient [m^2/s].

If absorptive and generating effects of gases are not taken into consideration, equation (6) can be expressed as:

$$N_a = -D_z \frac{dC_a}{dz} \tag{7}$$

where: N_a – gas flux [g/ m^{2}s].

In case LFG is no longer generated, equation (7) can be expressed as:

$$D_z = D \frac{\alpha_{gas}^{10/3}}{\alpha^2} \tag{8}$$

where: D – diffusion coefficient [m^2/s],
α_{gas} – gas porosity [-],
α – total porosity [-].

During downward movement, the relative density of carbon dioxide is 1.5 times higher than the relative density of air and 2.8 times higher than that of methane, so it tends to move downward, toward the landfill bottom.

Typical value of methane diffusion coefficient is 0.20 [cm^2/s] and of carbon dioxide 0.13 [cm^2/s].

Numerous factors influence gas movement, the most significant being: landfill design (including waste disposal facility construction), final cap design, measures taken to control gas movement, amount of generated gases, climate, and seasonal variations. Modern sanitary landfills minimize the probability of potential fires by covering waste, discarding the piles of incompatible wastes, and carefully controlling landfill gas generation.

5. METHANE PROPERTIES

Lower methane generation can be a result of the absence of anaerobic conditions for waste degradation in the landfill body, which are required for methane generation. Increased methane concentration in turn decreases oxygen concentration. The physicochemical properties of methane are shown in table 1.

Table 1 Physicochemical properties of methane

Properties	Values
Molecular mass	16.04 g/mol
Density	7,168 g/l
Melting/boiling/flash point	-183°C/-162°C/-188°C
Flammability limits	5-16%
Ignition temperature	650-750°C
Heat of combustion	56.19 MJ/kg
Flame colour	Pale blue
Gas colour	Colourless
Gas odour	Odourless
Solubility	Partially soluble in water Soluble in alcohol and ether

Methane is a naturally flammable and explosive component of LFG. Numerous reactions occur during methane combustion. Methane can participate in the formation of formaldehyde (HCHO), which in turn forms the formyl radical (•HCO), which then produces carbon monoxide. This process is better known as oxidative pyrolysis:

$$CH_4 + O_2 \rightarrow CO + H_2 + H_2O \tag{9}$$

During oxidative pyrolysis, H_2 oxidizes making water (H_2O) and releasing heat. This process is considerably fast, as it usually takes less than a millisecond:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{10}$$

Finally, CO oxidizes making CO_2 and releasing 282.9 [MJ/mol] or 12.64 [MJ/kg]. This process is typically slower than other partial chemical reactions in the entire process and usually takes several milliseconds:

$$2CO + O_2 \rightarrow 2CO_2 \tag{11}$$

The entire reaction of methane combustion can be expressed in the following manner:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O - 890 kJ/mol \tag{12}$$

6. TOTAL METHANE GENERATION

The calculation of landfill methane generation can be made using the following equation:

$$\begin{gathered} methane\ production = \\ \sum(methane\ emission + methane\ re\mathrm{cov}ery + methane\ oxidation) \end{gathered} \tag{13}$$

6.1. Methane emission

Methane emission is the release of methane into the atmosphere. From the emitter, i.e. the landfill, methane reaches the atmosphere where it disperses, transforms, undergoes deposition, and reaches the receptors. The only way to quantify strictly the efficiency of LFG/methane recovery is to measure the collected methane and the escaped methane emissions from the same landfill at the same time. Emitted methane is measured by means of any static chamber, such as the methane flux chamber or the closed flux chamber method, or by means of a research technique, such as the sampling point above-ground gradient technique or the eddy correlation technique. Gas emissions are measured with multi-gas detectors or with computerized gas analyzers.

6.2. Methane recovery

Methane recovery systems are either active or passive.

Active systems include vertical and horizontal wells containing a flow control valve and a gas sampling valve. Such systems are the most efficient.

Passive systems include sloped ventilation channels with gravel filling installed into the landfill body, gravel barriers, gravel-filled trenches, ventilation screens, and gas wells. These systems are used in shallow landfills and their installation and maintenance costs are very low. They operate on the principle of methane movement due to difference in pressure.

6.3. Methane oxidation

Methane oxidation depends on the following factors: temperature, humidity, nutrient availability, and soil type and structure. Data obtained by laboratory research are combined with methane emission measurements in the field in order to quantify oxidation at multiple locations at the landfill and then to extrapolate methane values over the entire landfill.

Microbiological methane oxidation is attributed to a group of microorganisms called methanotrophs. Methane oxidation is expressed with the following chemical reaction [9]:

$$\begin{gathered} CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + heat \\ \Delta G^\circ = -780 kJ/mol\ CH_4 \end{gathered} \tag{14}$$

Methane oxidation occurs in a relatively limited horizontal “layer”, where both methane and oxygen are available. Methane is generated in the landfill body, whereas oxygen is supplied through diffusion from the atmosphere. Laboratory testing of a simulated landfill showed that the active zone in terms of methane oxidation is in the upper layers, 30-40 cm above the landfill surface [4].

6.3.1. Climate and ambient conditions of soil temperature at the landfill

Methane oxidation rate increases with temperature, whereas low temperatures prevent oxidation. Optimal temperatures for methane oxidation range from 25 to 35°C. The temperature coefficient value Q_{10} is used to show how many times methane oxidation rate increases when temperature is increased by 10°C. The average value of Q_{10} is 1.88 ± 0.14 between 10 and 20°C. High Q_{10} values of 3.4 to 7.3 indicate that temperature is the dominant factor in methane oxidation in comparison to other factors.

6.3.2. Atmospheric pressure

The difference in pressure is one of the factors that control the horizontal gas flow through the landfill body. The decrease in atmospheric air pressure can “pump out” the gas from the landfill body. Some gas flow models utilize air pressure as the chief factor of gas transport through the soil. There is a very strong negative relationship between measured methane emissions and atmospheric air pressure.

Other factors, such as nutrient availability and physical properties of landfill cover materials, influence methane flow, which is how methane supply affects the oxidation rate.

7. LANDFILL GAS UTILIZATION

The positive effects of utilizing LFG are the following: ecologically, its reduction of the greenhouse effect; energy-wise, its use as a fuel for producing thermal or electric energy; economically, its ability to be sold in the market; and socially, its room for new biotechnologies in the newly-organized or “improved” landfills. Although methods and technologies for LFG utilization are available, they are still underutilized, mostly due to scarce legislation on LFG utilization and control.

The total LFG emission is calculated with the following equation [1]:

$$G_{total} = M_{total} \cdot \left(\frac{a \cdot 365 \cdot 24 \cdot 3600}{12} + \frac{b \cdot 365 \cdot 24 \cdot 3600}{12 \cdot 1.3} \right) \cdot 10^{-6} \tag{15}$$

where: G_{total} – total LFG emission [g/s],
M_{total} – peak LFG emission per second, [g/s],
a – warm season with temperatures above 8 ºC [months],
b – cold season with temperatures ranging from 0 to 8 ºC [months],
1.3 – growing inequality coefficient that considers irregular LFG generation during gas sampling during the cold season,
365, 24, 3600 – coefficients.

The period of active LG emission is calculated by the following equation:

$$t = \frac{10248}{T_{warm} \cdot t_{av.warm}^{0.301966}} \tag{16}$$

where: t – period of active LFG emission [t/year],
T_{warm} – warm season in observed areas [days],
$t_{av.warm}$ – average temperature in observed areas during warm seasons [ºC],
10248 and 0,301966 – specific coefficients for chemical degradation of organic waste mixture.

The difference between the methane emission prediction model and the actual measured amount of methane emitted from landfills is due to unknown parameters. Those parameters include the level of aerobic and anaerobic decomposition of nutrients, the quantity of microorganisms, inhibition due to waste toxicity, physicochemical interaction, etc.

8. MEASUREMENT RESULTS AND DISCUSSION

Vranje is the only municipality in Serbia with an operational landfill, “Meteris”, which mostly complies with the EU standards. The current landfill site covers the area of 6.23 [ha], with the landfill body covering 3.1 [ha], but with room for expansion. The design landfill life was estimated at 20 to 24 years. In the 2 [km] radius, there are no stationary healthcare institutions, natural spas, food manufacture facilities, railways, heritage structures and monuments, etc. There is no residential block in the vicinity of the landfill (figure 1). The distance to the nearest houses in the villages of Suvi Dol and Ranutovac is 1.250 [m], and only a handful of houses are located 380 [m] away from the landfill (the hamlet of Dorinska Mahala). Between the houses and the landfill there is a buffering green belt. The distance between the landfill and downtown Vranje is 5.8 [km].

Fig. 1 Position of the “Meteris” landfill, Vranje in relation to inhabited areas

Morphological composition of municipal waste deposited at the “Meteris” landfill is shown in table 2.

Table 2 Morphological composition of municipal waste at the "Meteris" landfill, Vranje

Component	Percentage in the total value (%)
Paper, cardboard	27
Glass	5
Rubber	3
Plastics	3
Litter	12
Textile	8
Metal refuse	3
Organic waste – food leftovers	25
Ashes, debris, slag	12
Other	2
Total	100

Vranje has the moderate continental climate gravitating towards the Mediterranean climate. The weather conditions in Vranje from March 1 to April 1, 2010, as shown in figure 2, indicate frequent fluctuations of temperature, air pressure, and wind speed and direction. Wind occurrence frequency in relation to urban areas of Vranje is of primary importance for the influence of methane propagation in ambient air. Snowmelt during springtime in part resulted in a decrease in temperature and an increase in waste moisture content, which caused higher methane generation.

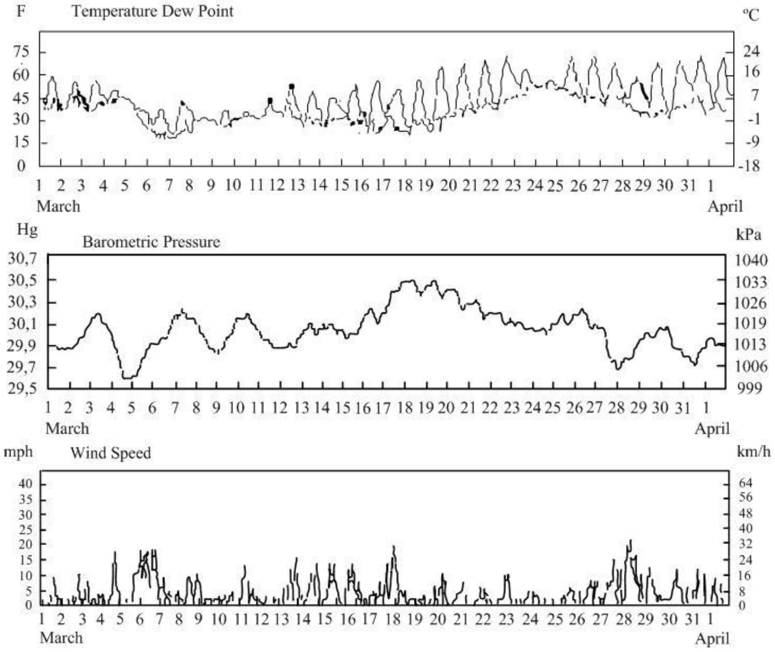

Fig. 2 Climatic condition values in Vranje from March 1 to April 1, 2010

We measured methane emissions from organic waste materials in the active sections of "Meteris" landfill on 24 gas wells [5]. The measures shown in table 3 are mean values of three measurements of methane concentration during stable landfill operation, which were conducted by means of the "MRU Vario Plus Industrial" gas analyzer.

Table 3 Results of methane emission measuring at the "Meteris" landfill, Vranje

Measuring point	Measured values (%)	Flammability limits (%)
Gas well 2	0.185	5-16
Gas well 3	0.380	5-16
Gas well 4	1.650	5-16
Gas well 5	1.250	5-16
Gas well 6	1.180	5-16
Gas well 8	1.230	5-16
Gas well 9	8.400	5-16
Gas well 10	8.200	5-16
Gas well 11	8.600	5-16
Gas well 12	6.200	5-16
Gas well 13	3.700	5-16
Gas well 14	2.200	5-16
Gas well 15	7.400	5-16
Gas well 16	7.700	5-16
Gas well 17	7.800	5-16
Gas well 18	8.900	5-16
Gas well 19	4.090	5-16
Gas well 20	0.900	5-16
Gas well 21	4.450	5-16
Gas well 22	4.450	5-16
Gas well 23	4.100	5-16
Gas well 27	0.190	5-16
Gas well 28	0.120	5-16

Based on the results of the analysis of methane generation on sample gas wells, the following conclusions can be drawn:

1 The content of waste accumulated at the "Meteris" landfill varies, with a noticeable landfill impact of climatic factors;
2. Physical, chemical, and biochemical processes in the observed gas wells vary;
3. The intensity of methane generation depends on the location of sample gas wells. Higher methane concentrations are generated on neighbouring, i.e. grouped gas wells, specifically on gas wells 9, 10, 11, and 12, as well as on gas wells 15, 16, 17, and 18;
4. Considering the measured methane concentrations, which are increased and within the flammability limits, there is a possibility of a fire outbreak at the landfill;
5. Pollution control, monitoring, and reporting on methane emissions are conducted through measurement and monitoring of landfill methane emissions.

8. CONCLUSION

The factors influencing the generation of methane as a landfill gas component include type of waste, size of deposited material, height of deposited waste, pH value, temperature, and moisture content. LFG, generated inside the landfill body, migrates along the path of least resistance through the soil or through the air (dispersion). LFG moves through the landfill body either upwards, by means of diffusion or convection, or downwards.

Total methane generation is determined in terms of methane emission, recovery, and oxidation. Measuring methane concentrations in landfills is important due to continuous monitoring of methane generation and its connection to fire outbreaks, the greenhouse effect, and the impact on human and environmental health.

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STVARANJE I PRAĆENJE METANA NA GRADSKOJ DEPONIJI

U radu su prikazane reakcije oksidacije metana kao dominantnog emitovanog gasa sa deponije, takođe su prikazane reakcije procesa oksidativne pirolize sa svim bitnim faktorima koji utiču na konačnu emitovanu količinu metana, kao što su: temperatura vazduha, temperatura tela deponije, pritisak, vlaga i struktura zemljišta. Na osnovu teoretskog saznanja i na osnovu emisionih meranja metana na deponiji „Meteris" Vranje, na 24 mernih mesta, vršena je analiza prekoračenja graničnih vrednosti metana u ambijentalnom vazduhu i mogućnost pojave požara usled dostizanja intervala zapaljivosti. Takođe, u radu su prikazane opšte karakteristike deponije „Meteris" Vranje

Ključne reči*: otpad, deponija, deponijski gas, metan*